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Chemistry Laboratory Manual for Bottom Sediments and Elutriate Testing

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Chemistry Laboratory Manual
for
Bottom Sediments and Elutriate Testing

U.S. Environmental Protection Agency
Surveillance and Analysis Division
Region V
Central Regional Laboratory
536 South Clark Street
Chicago, Illinois 60605
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This document contains the procedures which are used at the EPA, Region V, Central Regional Laboratory for the analysis of bulk sediments, elutriates and other solid samples.

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FORWARD

This manual contains the physical and chemical analysis procedures for bottom sediments and related process waters in partial fulfillment of the requirements of Section 404 (b) of Public Law 92-500, The Federal Water Pollution Control Act Amendments of 1972.

Most of the procedures in this manual are based on established standard methods, while others were developed (some published) by Region V, United States Environmental Protection Agency, Central Regional Laboratory personnel.

These procedures represent interim ones at best, but nevertheless provide some indication of the general chemical composition and pollutional nature of sediments.

The pollutional nature of bottom sediments, supplemented by results from elutriate testing are generally sufficient to enable managers and district engineers to decide whether the sediments should be "confined" or "open-lake" disposed.

Description of Field Sampling and Laboratory Handling Procedures

Sampling

1. Bottom sediment samples are generally collected by field personnel in such a manner that they are representative of the site from which they were collected. Petersen or Shipek-type collected samples are generally drained of excess water. Hopper-dredge collected samples generally contain more water than Petersen and other clam-type dredge-collected samples. Periodically, samples are collected using a core sampler.

2. Since the laboratory is now analyzing for trace organics, the sample should be collected either with a glass sampler or stainless steel one (no copper) manually mixed in the field, placed in a glass container and stored at 4°C (iced) until analysis. Sample containers should be filled only 3.4 full to prevent cracking when frozen.

3. If it is impossible to collect one sample for organics and inorganics, then it is acceptable to collect the trace organic samples with a metal sampler placed in a glass jar, and collect the inorganic sample with a plastic sampler and place in a plastic jar. This system may arouse questions of representativeness of sample, however.

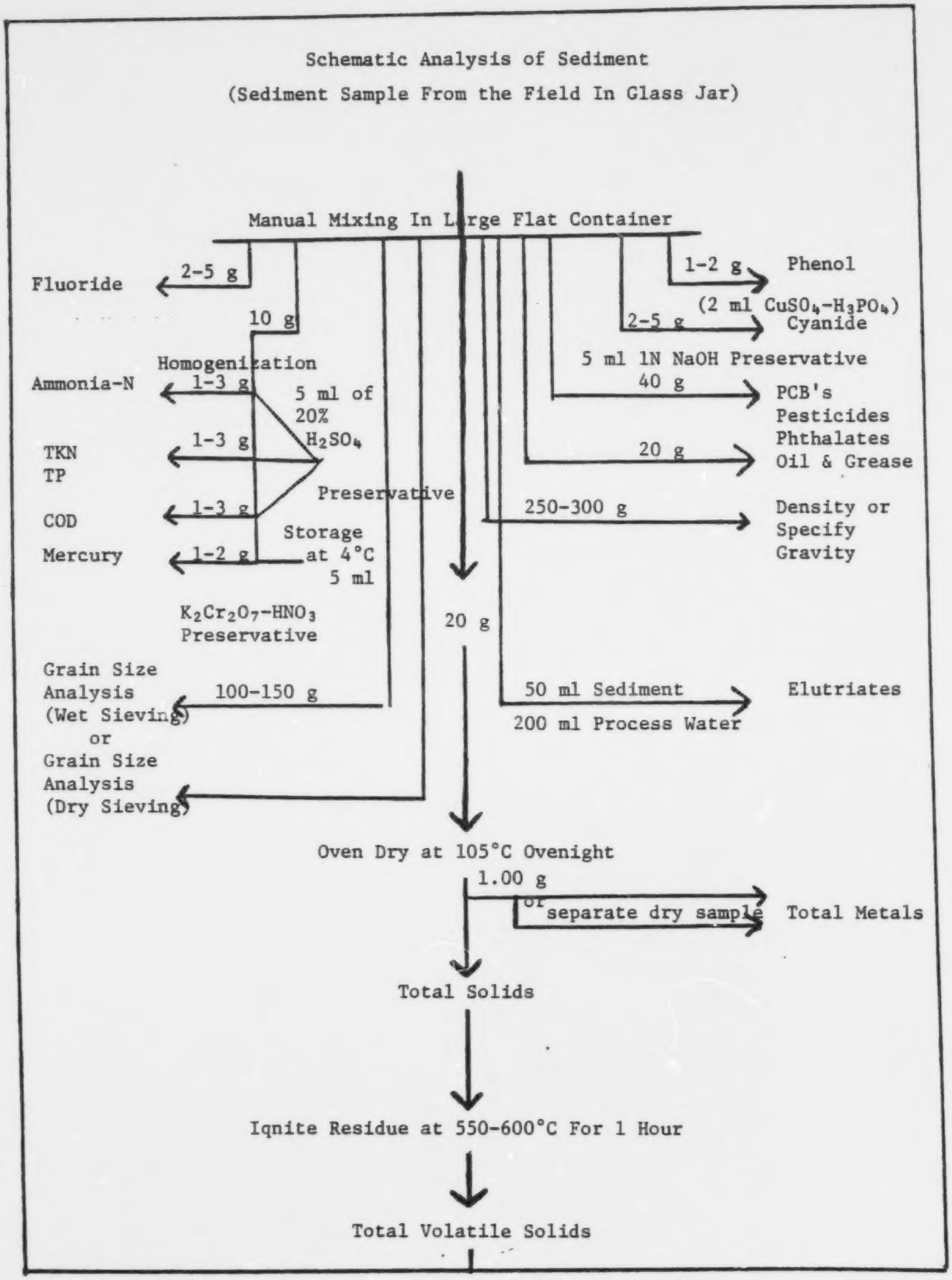
Laboratory Handling

1. Preservatives are not added to the sample, but the sample is kept between 2 and 4°C at all times in a walk-in refrigerator.

2. When the analyst is ready to proceed, the iced sample is allowed to thaw to 15-25°C. It is then manually mixed in a large flat bake-like or other contaminant-free containers and different fractions are weighed for the analysis listed in the schematic shown on the Figure. It is left up to the judgement of the analyst whther the sample should be sieved prior to weighing aliquots for analysis. If the sample does require sieving, it is passed through a #10 polypropylene sieve by forcing it through the screen with a glass beaker. A portion of the sieved sample is also taken for total solids. Any material retained by the sieve will be dried weighed and included in the total solids calculation as a dilution factor.

   Under no conditions is the sample for PCB's, phthalates and pesticides sieved. The total solids result from the unsieved sample is used to calculate dry weight for the unsieved trace organics.

3. All results are reported in milligrams per kilograms dry basis except solids, which are reported in percent.



Schematic Analysis of Sediment

(Sediment Sample From the Field In Glass Jar)

Manual Mixing In Large Flat Container
2-5 g
Fluoride
10 g
Homogenization
Ammonia-N
1-3 g
5 ml of
20%
H_2SO_4
TKN
TP
1-3 g
Preservative
COD
1-3 g
Storage
at 4°C
Mercury
1-2 g
5 ml
$K_2Cr_2O_7$-HNO_3
Preservative
Grain Size
Analysis
(Wet Sieving)
or
Grain Size
Analysis
(Dry Sieving)
100-150 g
20 g
1-2 g
Phenol
(2 ml $CuSO_4$-H_3PO_4)
2-5 g
Cyanide
5 ml 1N NaOH Preservative
40 g
PCB's
Pesticides
Phthalates
Oil & Grease
20 g
250-300 g
Density or
Specify
Gravity
50 ml Sediment
200 ml Process Water
Elutriates
Oven Dry at 105°C Ovenight
1.00 g
or
separate dry sample
Total Metals
Total Solids
Iqnite Residue at 550-600°C For 1 Hour
Total Volatile Solids

Figure

Determination of Total Residue of Sediments
CRL Method No. 444

Scope and Application

This method is applicable to the determination of percent residue in sediments and other solid samples.

Summary of Method

A portion of the unsieved sample is added to a tared evaporating dish and dried to constant weight at 105°C.

Equipment

Drying oven

Desiccator

Evaporating dishes

Five significant place blanace, 200 g capacity

Muffle furnace

Procedure

1. Tare the evaporating dishes by igniting them in the muffle furnace for one hour at 550 ± 50°C. Cool and place in a desiccator for a minimum of one hour.
2. Weigh the empty dishes to five figures (example - 90.345).
3. Place 10 to 20 grams of wet, well mixed sediment sample into the tared evaporating dishes (include all sticks and stones if the sample is not sieved). Record the weight of the sediment sample plus the evaporating dish. If the sample is sieved for other tests, use the weight of the sample which includes sticks and stones for final calculations.
4. Dry the sample at 105°C overnight or until constant weight is obtained.
5. Cool, place in desiccator for a minimum of 1 hour, then weigh.

Quality Control

A duplicate of one of the sediments is analyzed with each group of samples. If twenty or more samples are analyzed, a mininum of two duplicates are analyzed.

The analytical balance is calibrated and set to zero before each sample is weighed.

Calculations

Total Residue (%)

$$= \frac{\text{(Init wt. of sample and dish-final wt. of sample and dish-orig. sample wt.)}}{\text{(Original Sample Weight)}} \times 100$$

REFERENCE

Standard Methods for the Examination of Water and Wastewater, 14th ed., 1975, APHA, AWWA, WPCF, Washington, D.C. p. 91-92.

Determination of Total Volatile Solids in Sediments and Other Solids
CRL Method No. 447

Scope and Application

This method is an estimate of those inorganic and organic compounds which are lost from the sample when ignited to 550 ± 50°C.

Summary of Method

The volatile and fixed components remaining after the sample has been dried at 105°C are determined by igniting the dried sample in a muffle furnace at 550 ± 50°C. The loss in weight represents the amount of volatile matter in the sample.

Equipment

Porcelain evaporating dishes
Muffle furnace
Analytical balance (4 to 5 significant places)
Desiccator

Procedure

1. Record the weight of the sample and dish determined for total solids.

2. Ignite the residue from the total solids determination in a muffle furnace at 550 ± 50°C for one hour.

3. Remove carefully from the furnace, air cool for about one minute on a hard fire-proof finish (not the counter top) and place in a desiccator for a minimum of 15 minutes or until constant weight is obtained.

4. Ascertain whether constant weight has been attained by weighing the sample to 5 significant figures (examples 85.235) with no change in the fourth place.

Quality Control

A duplicate of one sample in each group of samples is analyzed. When there are twenty samples or more, a minimum of two duplicates are analyzed. The analytical balance is calibrated and set to zero before each sample is weighed.

$$\text{Total Volatile Solids (\%)} = \frac{[\text{wt. of dried solids - weight of ash}]}{[\text{weight of dried solids}]} \times 100$$

REFERENCE

1. Standard Methods for the Examination of Water and Wastes, 14th ed., 1975, pp. 95-98.

Determination of Percent Moisture of Sediments
CRL Method No. 445

Scope and Application

This method is applicable to the determination of moisture in sediments and other solid samples.

Summary of Method

A portion of the unsieved sample is added, to a tared evaporating dish and dried to constant weight at 105°C.

Equipment

Drying oven
Desiccator
Evaporating dishes
Five significant place balance, 200 g capacity
Muffle furnace

Procedure

1. Tare the evaporating dishes by igniting them in the muffle furnace for one hour at 550 ± 50°C. Cool and place in a desiccator for a minimum of one hour.

2. Weigh the empty dishes to five figures (example - 90.345).

3. Place 10 to 20 grams of wet, well mixed sediment into the tared evaporating dishes and record the weight of the sediment sample plus the evaporating dish.

4. Dry the sample at 105°C for 24 hours or until constant weight is obtained.

5. Cool, place in desiccator for a minimum of one hour, then weigh until constant weight is obtained.

6. Cool, place in desiccator for a minimum of one hour, then weigh.

Quality Control

A duplicate of one of the sediments is analyzed with each group of samples. If twenty or more samples are analyzed, a minimum of two duplicates are analyzed.

The analytical balance is calibrated and set to zero before each sample is weighed.

Calculations

$$\text{Percent moisture} = \frac{\text{initial wt. of sample \& dish} - \text{final wt. sample and dish}}{\text{Net weight of initial sample}} \times 100$$

or total residue in % - 100 = % moisture

REFERENCE

1. Standard Methods for the Examination of Water and Wastewater, 14th ed., 1975, a PHA, AWWA-WPCF, Wash., D.C. pp. 91-92.

Determination of Density of Sediments and Other Solids
CRL Method Number 446

Scope and Application

This method is applicable to all sediments and solids which contain visible amounts of water.

Summary of Method

A measured volume of the sediment-water is weighed on an analytical balance. Density is determined by the weight of the measured volume of the sample.

Equipment

Four or five significant place balance, 250 ml Erlenmeyer flask or bottle.

Procedure

1. Calibrate a 250 ml Erlenmeyer flask, by measuring 250 ml of distilled water into it and marking the 250 ml graduation level with a felt tip pen.

2. Shake all of the water out of the flask, and weigh the calibrated flask to the nearest 0.1 g.

3. Fill the flask completely to the marked graduated level with unsieved sample, record the weight. The volume is considered 250 ml. (If the sample does not flow readily, add as much sample to the flask as possible, and weigh. After weighing, mark the level to which the sample was poured, empty and rinse the flask. Refill the flask with distilled water to the marked level and re-weigh).

Quality Control

A duplicate of one of the samples is analyzed for each group of samples. If twenty or more samples are analyzed, a minimum of two duplicates should be analyzed.

The analytical balance is calibrated and set to zero before each sample is weighed.

Calculations

$$\text{Density} = \frac{[\text{weight of sample and flask - weight of flask}]}{[\text{volume of sample}]}$$

REFERENCE

1. Standard Methods for the Examination of Water and Wastes, 14th ed., 1975, p. 121.

Determination of Specific Gravity of Sediment and Other Solids
CRL Method No. 448

Scope and Application

This method is applicable to all sediments and solids which contain visible amounts of water.

Summary of Method

A weighted volume of sample is compared to an equal volume of distilled water.

Equipment

Four or five significant place balance, 250 ml Erlenmeyer flask or bottle.

Procedure

1. Weigh to the nearest 0.1 g, an empty wide mouth flask or bottle of about 250 ml capacity.
2. Fill the container completely with distilled water and weigh again.
3. Discard the distilled water and shake all of it out of the flask. Fill the flask or bottle completely with unsieved sample and re-weigh. (If the sample does not flow readily, add as much sample to the flask as possible, and weigh. After weighing, mark the level to which the sample was poured, empty and rinse the flask. Refill the flask with distilled water to the marked level and re-weigh).

Quality Control

A duplicate of one of the samples is analyzed for each group of samples. If twenty or more samples are analyzed, a minimum of two duplicates should be analyzed.

The analytical balance is calibrated and set to zero before each sample is weighed.

Calculations

$$\text{Specific Gravity} = \frac{[\text{wt. of sample and flask} - \text{wt. of flask}]}{[\text{wt. of distilled water and flask} - \text{wt. of flask}]}$$

REFERENCE

1. Standard Methods for the Examination of Water and Wastes, 14th ed., 1975, p. 121.

Determination of Settling Rates of Sediments and Other Solids
CRL Method No. 486

Scope and Application

This method is applicable to sediments, sludges and solid samples.

Summary of Method

The settling rate is obtained by measuring the suspended solids content of a 10 ml aliquot withdrawn from the original sample at 1, 3, 5, 10, 20 minutes, etc., time intervals. The suspended solids curve is determined and the values are plotted against time intervals. The settling rate is obtained from the slope of the linear portion of the curve. The Oden curve could also be obtained by plotting % suspended solid versus time.

Equipment

Timer.

Oxford pipett (10 ml capacity) with disposable tips.

Settling jar vessel long enough to hold 1-2 liter capacity with a wide mouth.

Filtration apparatus: suitable for the type of filter selected, with suction flask of 500 ml capacity and filter holder.

Glass filter disks:

Oven adjusted to 105°C.

Procedure

Weigh exactly 50-100 grams of well mixed sediment.

Transfer the sediment sample to the settling jar.

Add 1 liter of distilled water or preferably 1 liter of the natural (process) water [lake, river, lagoon] from which the sediment samples were taken.

Recap the jar and shake the sample by turning the jar upside down several times until a homogenous distribution is obtained.

Return the jar or vessel to an upright position. Open the lid and start the timer.

With the Oxford pipett equipped with special filter tips, [cut the narrow end of the tip to minimize filtration effect] withdraw a 10 ml aliquot from the middle of the sample bulk. [Withdrawal point could be fixed by allowing the Oxford pipett to descend to a certain length, already marked on the other pipett and aligned with vessel mouth.]

Transfer the aliquot to a 100 ml measuring cylinder with a glass cap.

Determine the suspended solids content of the sample using CRL Method number 441.

Construct an arithmetic plot of mg/l of suspended solids versus time and draw a line of best fit through the linear portion of the curve. The negative slope of such line will be the settling rate in mg/l/min.

Quality Control

To plot the Oden curve, calculate the % suspended solids by using the following formula:

$$\%\ \text{sus. solids} = \frac{[\text{sus. solids of aliquot-susp.solid of blk in mg/l}]}{\text{wt. of original sample (gm)} \times 10}$$

Plot % sus. solids versus time.

REFERENCES

1. Sedimentation Engineering Report, the American Society of Civil Engineers Manual, 1975.

2. American Society for Testing and Materials, "Method for Grain Size Analysis of Soil", D422-63, part 11, 1966, pp. 193-201.

3. Standard Methods for the Examination of Water and Wastewater, 14th ed, Amer. Public Health Association, New York, 1975, pp. 129-132.

Grain Size Analysis by Washing
(Approximate Estimation)
(Wet Sieving)
CRL Method #483

Scope and Application

This method is a fast and approximate estimation of grain sizes and applicable only to mud, sediments and clay samples.

Summary of Method

A sample is thoroughly homogenized and the excess water is poured off and drained. A wet weight of the sample is washed through a set of pre-weighed sieves and the % retained on each sieve is recorded (water content of sample is included.)

Apparatus

Top loading balance (1500 gram capacity)
A series of U.S. Standard sieves sizes 10, 20, 60 and 200.

Procedure

1. Remove non representative objects from the sample, such as large stones, debris, leaves, etc.
2. Drain the water accumulated on the top of the sample (as much as you can).
3. Thoroughly mix the sample, (use a metal spatula).
4. Weigh a 100 gm of sample (in a beaker).
5. Select the nest of sieves to be used. Weigh them and record the weight as sieve # tare weight.
6. Arrange them in descending order (pore size), with #200 at the bottom.
7. Transfer the sample to the top sieve and wash the sample with tap water until separation is complete.
8. Separate the sieves and let them stand for some time to drain the excess water.
9. Re-weigh the sieves with the particles retained on it.

Quality Control

A duplicate of one of the sediments is analyzed with each group of samples. If twenty or more samples are analyzed, a minimum of two duplicates are analyzed. A precision study by wet sieving technique is attached.

Calculations

The percent of material by weight retained on the various sieves is computed as follows:

$$\%\ \text{retained} = \frac{\text{sieve \# weight} - \text{sieve \# tare weight}}{\text{Total amount of sample}} \times 100$$

$$\%\ \text{passed \#200} = \frac{\text{total amt. of sample} - \text{amt. retained on all sieves}}{\text{Total amount of sample}} \times 100$$

Reference

United States Environmental Protection Agency, Region V, Central Regional Laboratory, Chicago, Illinois, 1976, unpublished.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE: February 23, 1977

SUBJECT: Precision Study of Sleve Test on Sediments

FROM: Harvey Montgomery, Chemist
Inorganic Chemistry Section, CRL

TO: Files

Four determinations of the sieve test were made on sediment samples from Les Chenaux Harbor. The samples of sediment were thoroughly homogenized for each test. Approximately 100 grams was weighed to the nearest gram. Number 10, 20, 60, and 200 sieves were placed in the sink. The samples was washed into the #10 sieve, thru #20, thru #60, and finally the #200 sieve, and then down the drain. Care was taken to avoid any material being washed over the side of the sieve.

The sample was pressed by my fingers so as much material was made to go through the sieve as possible. The sieves were weighed with an average amount of water on the sieve. This weight is constant. The sieves were weighed after the sample was washed. The amount of sample x 100 divided by the total weight is the percent retained.

The variation observed in percent retained is caused by several factors. The material is composed of rocks, organic material, clay, and sand.

Enclosure (data of study)

cc: B. Fairless, CRL

SIEVE TEST

1/19/77

SAMPLE #	AVE.	STD DEV	% RETAINED NO. 10	AVE.	STD DEV	% RETAINED NO. 20	AVE.	STD DEV	% RETAINED NO. 60
13597			3			K1			17
13597	5	2	6	2	1	2	11	5	9
13597			6			2			8
13598			4			5			24
13598	7	3	9	2	2	K1	19	4	16
13598			9			K1			19
13599			2			K1			7
13599	5	3	8	1	1	2	6	2	7
13599			6			K1			4
13601			2			K1			8
13601	4	3	7	2	1	3	10	2	13
13601			2			1			10

	AVE	STD DEV	%RETAINED NO. 200	AVE	STD DEV	%PASSED NO. 200
13597			25			55
13597	19	6	14	63	7	69
13597			18			66
13598			14			53
13598	10	4	7	61	8	63
13598			9			63
13599			20			71
13599	18	2	16	69	2	67
13599			19			71
13601			24			66
13601	23	2	21	61	5	56
13601			25			63

Grain Size Analysis (Dry Sieving)
CRL Method No. 485

Scope and Application

This method is applicable to sand, clays, sediments and soil samples. The method also covers the determination of materials finer than No. 200 sieve (by washing).

Summary of Method

A sample is dried and certain weight of the sample is first washed through #200 sieve. The loss in weight, resulting from the wash treatment, is calculated and is reported as the % passing #200. The amount retained on the #200 sieve is passed through a nest of sieves and the percentage of material retained at each sieve is calculated from the weight of material.

Definition

Grain size analysis is a process in which the percentage of material of each grain size present in given soils is determined by passing a known amount of the material through a set of sieves in order to separate the different particle sizes.

Apparatus

A series of U.S. standard sieves, 3/8, 4, 10, 16, 28, 50, 100, 200 bottom and cover plate (additional sieve #'s could be added).

Sieve shaker: a mechanical device to shake the sample with certain amplitude, usually equipped with a timer. (Model Fritsch Analysette or comparable to it)

Top load balance (1500 gm capacity) (0.1 gm sensitivity).

Soft wire brush.

Mortar and rubber covered pestle.

Oven adjusted to 105°C.

Procedure

1. Sample Preparation

   Thoroughly mix the sample (use metal spatula), remove non representative objects, such as large stones, debris, leaves, etc., add small amount of water to homogenize the sample if necessary.

2. Weigh 150-200 gm of the sample into a pre-weighed clean, dry crucible.
3. Oven dry the sample at 105°C to a constant weight (preferably overnight).
4. Allow to cool.
5. Transfer the sample to a piece of heavy paper. Loosen the aggregates with hands or use the Mortar and Rubber pestle if necessary.
6. Weigh 100 grams of the dry sample (use clean porcelain dish or beaker).
7. Transfer this amount to #200 sieve other than the one to be used with the nest of sieves.
8. Wash the sample with tap water in order to pass through those particles which are finer than the #200 sieve; then with distilled water.
9. Oven dry the amount of sample retained on the #200 sieve (the #200 sieve with the material can be placed directly into the oven at 105°C).
10. Transfer the amount retained on #200 sieve to a pre-weighed beaker by turning the sieve over and brushing the back with the wire brush (use a funnel if necessary.
11. Weigh this amount and record as total amount retained by #200.
12. Select a nest of sieves, weigh them and record the tare weights as sieve # tare weights.
13. Place the nest of sieves in the shaking machine in the following descending order: 3/8, 4, 10, 16, 50, 100, 200 and the bottom plate.
14. Pour the amount retained on #200 sieve on the top sieve (3/8). Secure the cover plate (tighten screws).
15. Adjust timer to 15 minutes.
16. Turn on the shaker with an amplitude of 10.
17. After the shaking time is over, remove the nest of sieves from the shaker. Beginning with the top sieve, weigh it on the balance and record the weights as sieve # weight.

Quality Control

A duplicate of one sample is analyzed with each group of samples. For twenty or more samples, a minimum of two duplicates are analyzed.

The analytical top load balance is set to zero before each weighing.

Experimental recovery data are attached for the dry sieve procedure.

Calculations

The percent of material by weight retained on the various sieves is computed as follows:

$$\text{Percent retained} = \frac{\text{sieve \# weight - sieve \# tare weight}}{\text{TOTAL amount of sample}} \times 100$$

$$\text{Percent passed \#200} = \frac{\text{TOTAL amount of sample - total amt. ret. \#200}}{\text{TOTAL amount of sample}} \times 100$$

REFERENCES

1. American Society for Testing and Materials (ASTM), "Standard Method or Test for Sieve or Screen Analysis of Fine and Coarse Aggregates", Designation C 136-71, American National Standard A378, Sept. 1971, pp. 87-88

2. American Society for Testing and Materials (ASTM), "Standard Method or Test for Materials Finer than No. 200 (75-um) Sieve in Mineral Aggregates by Washing", Designation C117-69 American National Standard A374, 1970, October 1969, pp. 68-69.

Sample #	% Rtd #3/8	% Rtd # 4	% Rtd # 10	% Rtd # 16	% Rtd # 28	% Rtd # 50	% Rtd # 100	% Rtd # 200	% passed pass 200	% Recovery TOTAL
GLSB (169)										
72-6753	0	0	0.65	0.65	0	0.65	0.65	76.2	21.2	100
72-6756	0	6.1	9.6	7.6	23.3	13.1	16	6.9	11.5	94.1
72-6757	0	3.2	12.3	6.6	14	30	19.8	6.9	5.9	98.7
72-6763	19.8	8.2	16	5.8	16.9	9	7.2	3.8	11.3	98
GLSB (170)										
EGS01	3.6	6.6	6.2	3.4	4.9	7.4	28	20	18.4	98.5
EGS02	0.0	0.3	4.7	2.8	6.4	7.7	28	23	26	98.9
EGS03	0	3	9.5	11	17	2.6	.4	.2	55.3	99
EGS04	4.8	4.5	8.6	11.9	22.4	5.7	2.1	1	38	99
EGS05	0	0.3	8	9.5	23.6	6.3	1.5	.5	48.3	98
EGS06	0	0	1.9	3.3	5.5	1.3	.4	1.7	85.8	99.9

Determination of Fluorides in Sediments
and Other Solids
CRL Method #380

Scope and Application

This method is applicable to the measurement of fluoride in sediments and other solids (other than glass fiber filters).

Summary of Method

Fluoride is determined by manual distillation of the sediment sample at 180°C from 50% sulfuric acid solution followed by potentiometric analysis using a fluoride selective ion electrode.

Equipment

500 ml or 1000 ml flat bottom distilling flask equipped with a thermometer adaptor and Graham or other condenser.

Erlenmeyer Flask

Analytical Balance

Specific Ion Meter (See CRL Method #378, Attached)

Fluoride Specific Ion Electrode (See CRL Method #398, Attached)

Reagents

Sulfuric Acid, Concentrated

Buffer Solution (See CRL Method #378, Attached)

Procedure

1. In a 500 ml boiling flask, carefully add with stirring 100 ml of concentrated sulfuric acid to 200 ml of distilled-deionized water.

2. Distill into an Erlenmeyer flask until the contents of the boiling flask reaches 180°C. Discard the distillate.

3. Cool the acid mixture remaining in the flask to 90°C.

4. Add 2 to 5 grams of wet, well mixed sediment sample.

5. Mix throughly and distill until the temperature reaches 180°C. Do not exceed 180°C to prevent Sulfate carryover.

   Note: If the sample is known to have a high chloride content, add silver sulfate to the fask at the rate of 5 mg Ag2SO4 per

   milligram of chloride in the sample.

6. Place 25 ml of the distillate in a 100 ml beaker and add 25 ml of buffer. Place on a magnetic stirrer and mix at medium speed. Immerse the probe in the solution and observe the meter reading while mixing (See CRL Method #378, Attached).

7. Allow the probe to remain in the solution for at least three (3) minutes or until the reading has stabilized. (At lower concentrations below 0.50 ppm, it sometimes takes 5 minutes to reach a stable meter reading.

8. Read the fluoride level of the sample directly in mg/l on the fluoride scale.

Quality Control

A field reagent blank (which contains 200 ml of distilled-deionized

water and 100 ml of Conc. H_2SO_4), one or two F^- standards and a duplicate of one of the samples are distilled and analyzed for each group of samples. If twenty are more samples are analyzed a minimum

of two field blanks, F^- standards and duplicates are distilled and analyzed.

The analytical balance is set to zero before each weighing.

The manufacturer's instructions are followed concerning operation of the specific ion meter.

Calculations

$$\text{mg/kgF}^- \text{ (dry basis)} = \frac{\text{mg/l Reading from Method \#378 x ml of sample used}}{\text{Orig. wet wt. in grams x decimal fraction \% solids}}$$

References

1. "Standard Methods for the Examination of Water and Wastewaters, p. 171, Method No. 121 A, Preliminary Distillation Steps (Bellack), 13th Edition, 1971.

2. Manual of "Methods for Chemical Analysis of Water and Wastes", Office of Technology Transfer, Washington, DC, 1974, p. 65.

Fluoride (Electrode) in Waters

CRL Method No. 378

Scope and Application

This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.

Concentrations of fluoride from 0.10 up to 1000 mg/l may be measured.

The Bellack distillation must be performed on industrial waste samples prior to electrode analysis.

Summary of Method

The fluoride is determined potentiometrically using a selective ion fluoride electrode in conjunction with a selective ion meter having a direct concentration scale for fluoride.

The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions.

Interferences

A high pH interferes; sample pH should not be greater than 10. polyvalent cations of Si+4, Fe+3, B+3, and Al+3 interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong, chelating agent, preferentially complexes aluminum (the common interference), iron, and eleminates the pH problem.

Apparatus

Specific ion meter such as the Orion model 407.
Fluoride combination electrode, such as Orion no. 96-09-00.
Magnetic mixer, Teflon coated stirring bars.

Reagents

Sulfuric acid, concentrated.
Buffer solution, pH 5.0 - 5.5: To approximately 500 ml of distilled water in a 1 liter beaker add 57 ml of glacial acetic acid, 58g of sodium chloride and 2g of sl,2-cyclohexylene dinitrilo tetraacetic acid (CDTA) (Mathieson, coleman & Bell, Cat. No. P8661) or cyclohexane diamine tetraacetic acid (Merck-Titriplex IV or Baker Cat. No. G083). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1 liter volumetric flask and dilute to volume with distilled water. For work with brines, additional sodium chloride should be added to raise the

chloride level to twice the highest expected level of chloride in the sample. Sodium fluoride, stock solution: Dissolve 0.2210g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. 1.0 ml = 0.1 mg fluoride. Store in polyethylene. Sodium fluoride, standard solution: Dilute 50 ml of sodium fluoride stock solution to 500 ml with distilled water. 1.0 ml = 0.01 mg/ml fluoride.

Calibration

Check zero adjustment: With the Function Switch in the off position, the needle should point to exactly center scale (1.0). If not, turn the zero adjust screw until the needle is exactly on center scale.

Check batteries: Turn Function Swith to the battery position. If the needle does not stop in or to the right of the green battery ok area on the meter, replace batteries. However, the meter is line operated in the laboratory.

Prepare three standards containing 0.40, 1.0 and 4.0 mg/l by pipetting 20,50 and 200 ml of standard fluoride solution into three 500 ml volumetric flasks and make up to volume with distilled water. Store standards in polyethylene bottles and store at room temperature. These standards are stable at room temperature.

Pipette 25 ml of each of the standards into a 100 ml beaker and add 25 ml of buffer solution. Place the 1 mg/l standard on the magnetic stirrer, the probe in the solution and stir for five minutes. If the meter does not read 1 mg/l, adjust by means of the calibration control knob to read 1 mg/l.

Follow same procedure for the 0.40 mg/l standard. If the meter does not read 0.40 mg/l, turn temperature compensator knob until the needle points to 0.40 mg/l. Move the slope indicator until the arrow of the temperature compensator points to the temperature of the solution.

Follow same procedure for the 4.0 mg/l standard. The meter should read very close to 4.0 mg/l or within 0.10 or 0.20 mg/l.

Procedure

Waste Samples:

1. Place 400 ml of distilled water into a one liter distilling flask and add 200 ml of concentrated sulfuric acid, with stirring. Distill until the contents of the flask reaches exactly 180°C. Discard the distillate. This process serves to remove fluoride contamination and adjust the acid-water ratio for subsequent distillations.

2. After cooling the acid mixture remaining from the steps outlined in step 1, or previous distillations, to 90°C or below, add 100 ml of sample, mix thoroughly, and distill as before until the temperature reaches 180°C. To prevent sulfate carry-over, do not permit the temperature to exceed 180°C.

3. Use the sulfuric acid solution repeatedly until the contaminants from the samples accumulate to an extent that recovery is affected or interferences appear in the distillate. Check suitability of the acid periodically by distilling standard fluoride samples.

4. Place 25 ml of the distillate in a 100 ml beaker and add 25 ml of buffer. Place on a magnetic stirrer and mix at medium speed. Immerse the probe in the solution and observe the meter reading while mixing. The probe must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.50 mg/l, it may require as long as five minutes to reach a stable meter reading. Read the fluoride level in the unknown directly in mg/l on the fluoride scale.

5. Drinking and surface waters.
   Place 25 ml of sample in a 100 ml beaker and add 25 ml of buffer solution. Then follow the procedure described in step 4.

Quality Control

A blank and duplicate of one of the samples is analyzed with each group of samples. If twenty or more samples are analyzed, a minimum of two blanks and standards ar analyzed.

Precision

The precision between-runs is 0.04 mg/l.
The precision within-runs is 0.03 mg/l.
These precision values were taken from Quality Control Data for the period February 2, 1975 thru June 2, 1975 consisting of eighteen analyses.

Calculations

Reading is directly in mg/l on the specific ion meter providing 25 ml of sample is used.

References

Manual of Methods for Water and Wastes, U.S. Environmental Protection Agency, Office of Technology Transfer, Washington, DC, 1974, pp. 65-67.

Determination of Total Cyanides in Sediment and Other Solids
CRL Method No. 366

Scope and Application

This method is applicable to the determination of cyanide in sediments and other solids.

Summary of Method

Cyanide is released from its compounds and converted to HCN by means of a reflux-distillation catalyzed by copper chloride which decomposes metallic cyanide complexes. The cyanide is absorbed in a 0.2 N NaOH solution and analyzed spectrophotometically using an automated system. The color reaction is based on reaction of cyanide with chloramine-T to form cyanogen chloride ($CNCl^-$) followed by reaction of the $CNCl^-$ with pyridine-barbituric acid to form at red color at 578 nm.

Equipment

Reflux distillation apparatus consisting of one liter or 500 ml boiling flask with inlet tube and condenser.

Technicon AA II System (See CRL Method No. 360, Attached)

Heating Mantles or Burners

Analytical Balance

Reagents

6N NAOH

Cuprous Chloride, 2%, Acid Washed (See CRL Method 360)

Sulfuric Acid Concentrated

Chloramine-T Solution - (See CRL Method No. 360)

Pyridine-Barbituric Acid Solution

Procedure

1. Weigh 2-5 g of wet, well mixed sediment.

2. Transfer to the distillation flask.

3. Add 500 ml of distilled water and 5 ml of 6 N NaOH to the flask.

4. Add 50 ml of 1.25 NaOH to the gas absorbing tube and dilute until the spiral is cover.

5. Connect the boiling flask, condenser and absorber, turn on the condenser cooling water and heating mantle.

6. Slowly add 25 ml of conc. H_2SO_4 through the air inlet tube. Rinse, allow 3 minutes for the acid to mix with the sample, then pour 10 ml of copper chloride ($Cu_2\ Cl_2$) solution into the inlet tube and rinse with distilled water.

7. Heat the solution to boiling, taking care to prevent the solution from backing up into the air inlet tube.

8. Reflux for one hour.

9. Turn off the heat and continue the air flow for 15 minutes. After cooling the boiling flask, disconnect the absorbes and turn off the vacuum.

10. Drain the solution from the absorber into a 250 volumetric flask. Rinse the distillation train into the flask and dilute to 250 ml.

11. Store under refrigeration until colorimetric analysis is conducted using CRL Method 360, (Attached).

Quality Control

One field reagent blank (which contains 5 ml of 6N NaOH), one standard and one duplicate are distilled and analyzed with each group of samples. If twenty samples are analyzed, a minimum of two blanks, standards and duplicates are distilled and analyzed.

The balance is set to zero before each sample is weighed.

The manufacturer's instructions are followed for operation of the Technicon Autoanalyzer.

Calculations

$$\text{mg/kg CN}^- \text{ (dry basis)} = \frac{\text{mg/l (from curve using Method 360) x 250}}{\text{(orig. wet wt of sediment in grams)xdecimal fraction of \% solids)}}$$

Reference

1. Manual of "Methods for Chemical Analysis of Water and Wastes", United States Environmental Agency, Office of Technology Transfer 1974, Washington, DC, pp 40-46.

Total Cyanide
CRL Method No. 360
(Automated Pyridine-Barbituric Acid With Manual Distillation)

Scope and Application

This method is applicable to the determination of cyanide in drinking, surface, saline, domestic and industrial waste waters.

Summary of Method

Cyanide is released from its compounds and converted to HCN by means of a reflux-distillation. It is absorbed in a solution of NaOH. This solution is then analyzed spectrophotometrically using an automated system.

In the spectrophotometric determination, the cyanide reacts with chloramine-T at a pH of <8 to form CNCl. Addition of a pyridine - barbituric acid reagent produces a red color which absorbs at 578 nm.

Sample Handling and Preservation

Samples are collected in new polyethylene bottles.

Samples are preserved at the time of collection by the addition of 5 ml of 6N NaOH/l of sample (pH $\geq$12). Samples are immediately cooled to 4°C for storage.

Samples should be analyzed as soon as possible after collection.

Interferences

Interferences are eliminated or reduced by following the distillation procedure described in step 1.

Sulfides adversely affect the colorimetric procedure. After distillation, samples are treated with a small amount of cadmium carbonate. If the sample contains sulfide, as indicated by a precipitate of yellow cadmium sulfide, additional cadmium carbonate is added just until precipitation is complete. Only the supernatant is taken for analysis.

If residual chlorine is present in the sample, an excess of $NaAsO_2$ is added to reduce the chlorine before distillation.

Equipment

Reflux distillation apparatus consisting of 1ℓ boiling flask with inlet tube and condenser, plus a gas absorber.

Heating mantles.

Powerstats, 10 amps & 120 volts.

Technicon Auto Analyzer II (3)

Sampler III or IV

Pump II or III

Cyanide cartridge

Colorimeter with 15 mm flowcells and 570 nm filters.

Recorder

Digital Printer

Reagents

1.25 N sodium hydroxide: Dissolve 50 g of NaOH in distilled water. Cool and dilute to 1ℓ.

Cadmium carbonate: powdered reagent.

Sodium arsenite: powdered reagent.

Cuprous chloride: Weigh 20 g of finely powdered $Cu_2 Cl_2$ into an 800 ml beaker. Wash twice with 250 ml portions of (1:49) H_2SO_4 and then twice with distilled water. Add 250 ml of distilled water and then 120 ml of conc HCl. Continue to add HCl as necessary for dissolution. Dilute to 1ℓ with distilled water and store in a tightly stoppered bottle or flask containing copper metal which extends the entire length of the container.

Sulfuric acid: Concentrated

Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g of KOH in 1ℓ of distilled water. Standardize with 0.0192 N $AgNO_3$ as described in Standard Methods (2). Dilute to the appropriate concentration so that 1 ml = 1 mg CN.

Standard cyanide solution (intermediate): Dilute 10 ml of Stock cyanide solution plus 10 g of NaOH to 100 ml with distilled water (1 ml = 0.1 mg CN). Store at 4°C.

Working standards: Dilute 0, 0.5, 1.0 and 2.0 ml of intermediate standard plus 10 g of NaOH to 1ℓ with distilled water for standards of 0, 0.050, 0.100 and 0.200 mg CN/l. Store at 4°C.

Standard silver nitrate solution, 0.0192 N: Prepare by crushing about 5 g of $AgNO_3$ crystals and drying to constant weight at 40°C. Dissolve 3.2647 g of dried $AgNO_3$ in distilled water and dilute to 1ℓ (1 ml $\doteq$ 1 mg CN).

Rhodanine indicator: Dissolve 20 mg of p - dimethyl - amino - benzalrhodanine in 100 ml of acetone.

Phosphate buffer: Dissolve 138 g of $NaH_2 PO_4 \cdot H_2O$ in distilled water and dilute to 1ℓ. Add 0.5 ml of Brij-35. Store at 4°C.

Chloramine - T solution: Dissolve 0.4 g of chloramine - T in distilled water and dilute to 100 ml. Prepare daily.

Pyridine - barbituric acid solution: Transfer 15 g of barbituric acid into a 1ℓ volumetric flask. Add about 100 ml of distilled water and swirl the flask. Add 75 ml of pyridine and mix. Add 15 ml of conc HCl and mix. Dilute to about 900 ml with distilled water and mix until the barbituric acid is dissolved. Dilute to 1ℓ with distilled water. Store at 4°C.

Sampler Wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

Procedure

Manual distillation

1. Add 50 ml of 1.25N NaOH to the gas sabsorbing tube and dilute with distilled water until the spiral is covered.

2. Measure 500 ml of sample into the boiling flask. Also distill one blank, one standard, and one duplicate with each set.

3. Connect the boiling flask, condenser, and absorber. Turn on the condenser water.

4. Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that about one bubble of air per second enters the boiling flask through the air inlet tube. NOTE: The vacuum will need to be readjusted occasionally to maintain this rate.

5. Slowly add 25 ml of conc H_2SO_4 through the air inlet tube. Rinse the tube with distilled water. Allow the acid to mix with the sample for 3 min. Then pour 10 ml of Cu_2Cl_2 reagent into the inlet tube and rinse the tube with distilled water.

6. Heat the solution to boiling, taking care to prevent the solution from backing up into the air inlet tube. Reflux for one hour. Turn off the heat and continue the air flow for 15 min. After cooling the boiling flask disconnect the absorber and turn off the vacuum.

7. Drain the solution from the absorber into a 250 ml volumetric flask. Wash the absorber with distilled water and add the washings to the volumetric flask. Dilute to 250 ml. Samples may be stored for future spectrophotometric analysis.

8. Set up the Auto Analyzer II as shown in the diagram.

9. Calibrate the system using standards of 0.200, 0.100, 0.050 and 0 mg CN/1. Analyze control standards CS1 and CS2, then analyze the distilled samples.

Detection Limit

The detection limit is 0.005 μgCN/l.

Quality Control

A blank, one standard and a duplicate are distilled with each sample set. The results are recorded in the QC book.

Control standards CS1 and CS2, a blank, and one duplicate are analyzed every 40 samples. They must be within control limits if the data is used. The results are recorded in the QC book.

The date of preparation of all reagents and standards is recorded in the QC book.

Calculations

The concentrations of calibration standards and control standards in μg/l are obtained directly from the Digital Printer.

Twice the concentration of the distilled sample in μg/l is obtained from the Digital Printer. (The concentration factor of 2 is the result of having distilled 500 ml of sample into 250 ml). The results obtained on the print-out must be divided by two.

The cyanide concentration must be reported as mg CN/l. This is obtained by dividing the μg/l concentration by 1000.

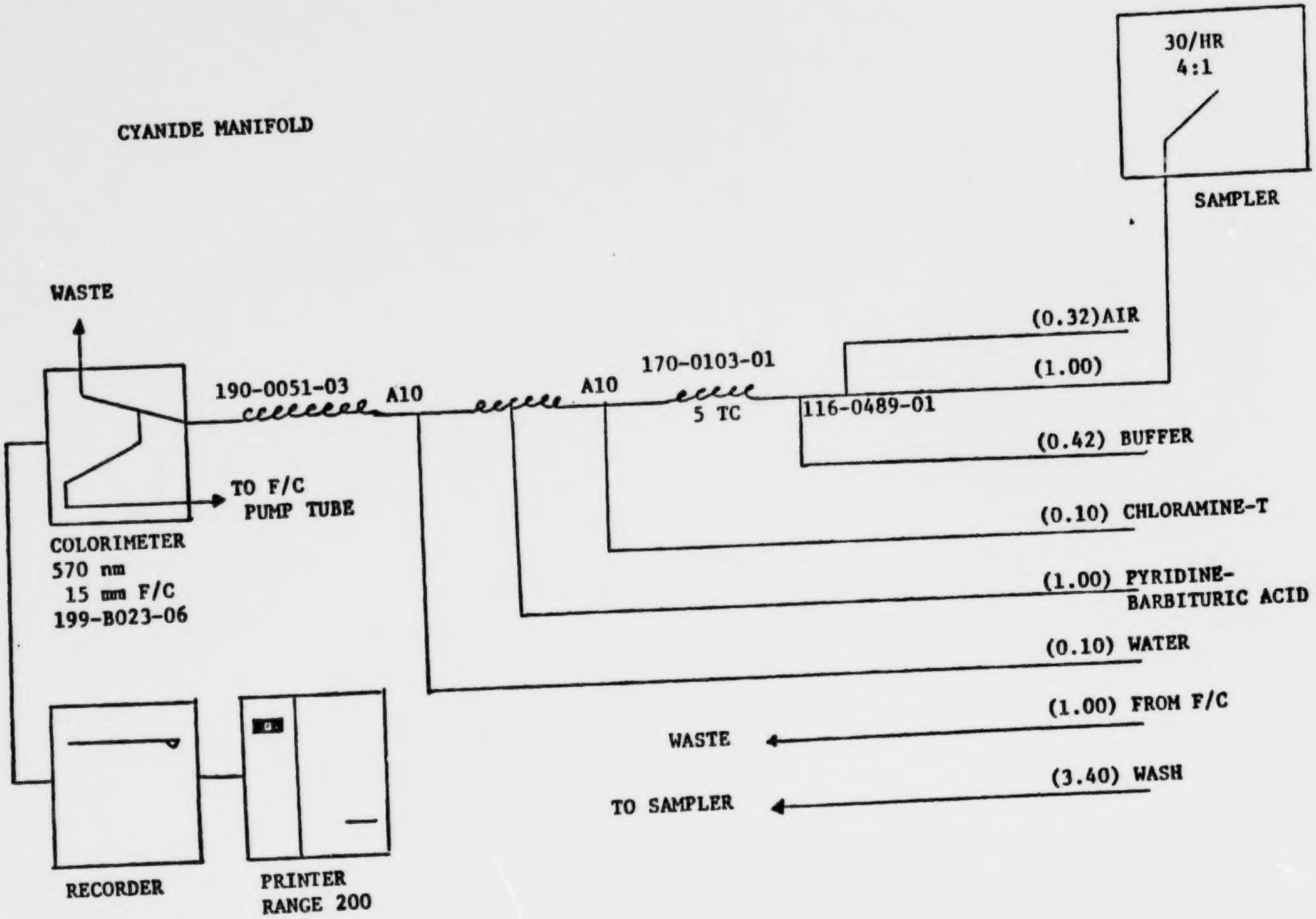
References

1. "Manual of Methods for Chemical Analysis of Water and Wastes", U.S. Environmental Protection Agency, Cincinnati, OH, 1975, p. 40.

2. "Standard Methods for the Examination of Water and Wastewater", 14th ed., American Public Health Association, New York, N.Y., 1975, p. 361.

3. Technicon industrial method no. 315-74W, Technicon Industrial Systems, Tarrytown, N.Y., 1974.

CYANIDE MANIFOLD


30/HR
4:1
SAMPLER
WASTE
190-0051-03
A10
A10
170-0103-01
5 TC
116-0489-01
(0.32)AIR
(1.00)
(0.42) BUFFER
(0.10) CHLORAMINE-T
(1.00) PYRIDINE-
BARBITURIC ACID
(0.10) WATER
(1.00) FROM F/C
(3.40) WASH
WASTE
TO SAMPLER
TO F/C
PUMP TUBE
COLORIMETER
570 nm
15 mm F/C
199-B023-06
RECORDER
PRINTER
RANGE 200

Determination of Cyanide
in Water and Wasteswater
(Completety Automated Procedure)
CRL Method No. 357

Scope and Application

The procedure is applicable to cyanide in water and wastewater. It is generally used at this laboratory only following the elutriate test and for the analysis of lake waters. Presently, it is not used for the analysis of wastewaters which are governed by the National Pollution Discharge Elimination System (NPDES) Permit.

Summary of Method

Cyanide is determined using a completely automated system. A UV digestion is incorporated in the automated distillation step which converts complex cyanides to simple cyanides. The solution is acified to form HCN which reacts with chloramine-T to form cyanogen chloride, followed by reaction with pyridene-barbituric acid to form a red-colored complex, which is read at 570 nanometers. An average 30 samples per hour can be analyzed in the range from 5 to 200 micrograms per liter.

Equipment

Technicon AA II system, equipped with UV digestor, Sample IV, Pump III or IV, and Colorimeter.

Reagents

Distillation Reagent
(Technicon No. 501-5017)

Phosphoric Acid, 85% (H_3PO_4)	250 ml
Hypophosphorus Acid	50 ml
Distilled Water, q.s.	1000 ml

Preparation: Carefully add 250 ml of 85% phosphoric acid and 50 ml of hypophosphorus acid to 700 ml of distilled water and dilute to one liter with distilled water.

Phosphate Buffer, pH 5.2

Potassium Dihydrogen Phosphate (KH_2PO_4)	13.6 g
Disodium Hydrogen Phosphate (Na_2HPO_4)	0.28 g
Distilled Water, q.s.	1000 ml
Brij-35* (Technicon No T21-0110)	0.5 ml

Preparation: Dissolve 13.6 g of potassium dihydrogen phosphate and 0.28 g of disodium phosphate in 900 ml of distilled water and dilute to one liter. Add 0.5 ml of Brij-35 and mix.

Chloramine-T

Chloramine-T** ($C_7H_7ClNO_2SNa \cdot 3H_2O$)	2.0 g
Distilled Water	500 ml

Preparation:

Dissolve 2.0 g of chloramine-T in 500 ml of distilled water.

Pyridine Barbituric Acid Reagent

Barbituric Acid ($C_4H_4N_2O_3$)	15 g
Pyridine (C_5H_5N)	75 ml
Hydrochloric Acid, conc. (HCl)	15 ml
Distilled Water, q.s.	1000 ml

Preparation:

Place 15 g of barbituric acid in one liter beaker and add enough water (about 100 ml) to wash the sides of the beaker and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of HCl (sp. gr. 1.19) and mix. Dilute to about 900 ml with distilled water and mix until all the barbituric acid has dissolved. Transfer the solution to a one liter flask and dilute to volume with distilled water.

Standards

Stock Standard A, 100 mg/l

Potassium Cyanide (KCN)	0.250 g
Sodium Hydroxide, 0.1N ($NaOH$), q.s.	1000 ml

Preparation: Dissolve 0.250 g of potassium cyanide in 800 ml of 0.1 N sodium hydroxide and dilute to one liter with 0.1 N of sodium hydroxide.

WARNING: AVOID SKIN CONTACT WITH POTASSIUM CYANIDE.

Stock Standard B, 10 mg/l

Dilute to 100 ml of stock A to one liter with 0.1 N sodium hydroxide.

Working Standards

ml Stock B	ug/l
1	100
2	200
3	50

Preparation: Pipette stock B into a 100 ml volumetric flask and dilute to volume with 0.01 N sodium hydroxide.

Procedure

1. Set temperature of the heating bath at 150°C.

2. Set the flow rate of the cooling water through the distillation apparatus at approximately 750 ml per minute at 14°C. (See Instruction Manual TAl-0213-00 for operation of distillation head).

3. Position the controls of the Modular Printer as follows:

Control	Position
Mode Switch	Normal
Sampling RATE Switch	30
Range Switch	200
Decimal Swith	000

(See Technical Publication No. TAl-0278-10)

4. Do not use the Modular Printer without a Linearizer. (The chemistry is linear up to 200 ug/l lnt a linearizer is needed for a linear response over the whole range).

5. Alternate ranges may be obtained by utilization of the Std. Cal. Control on the Colorimeter.

6. Make sure enough sodium hydroxide is added to the waste containers to keep the highly toxic HCN from escaping.

7. Analyze the samples using the attached manifold with a 0.01 N NaOH wash.

8. When installing replacement light source in UV Digestor, allow burn-in of 12 to 24 hours to permit new UV lamp to equilibrate. (New lamps may generate undesirable levels of ozone, which may cause lower cyanide results.

Quality Control

A field reagent blank and duplicate are analyzed with each group of samples. If twenty or more samples are analyzed a minimum of two blanks and duplicates are analyzed.

The Technicon Company Instructions are followed for operation of the instrument.

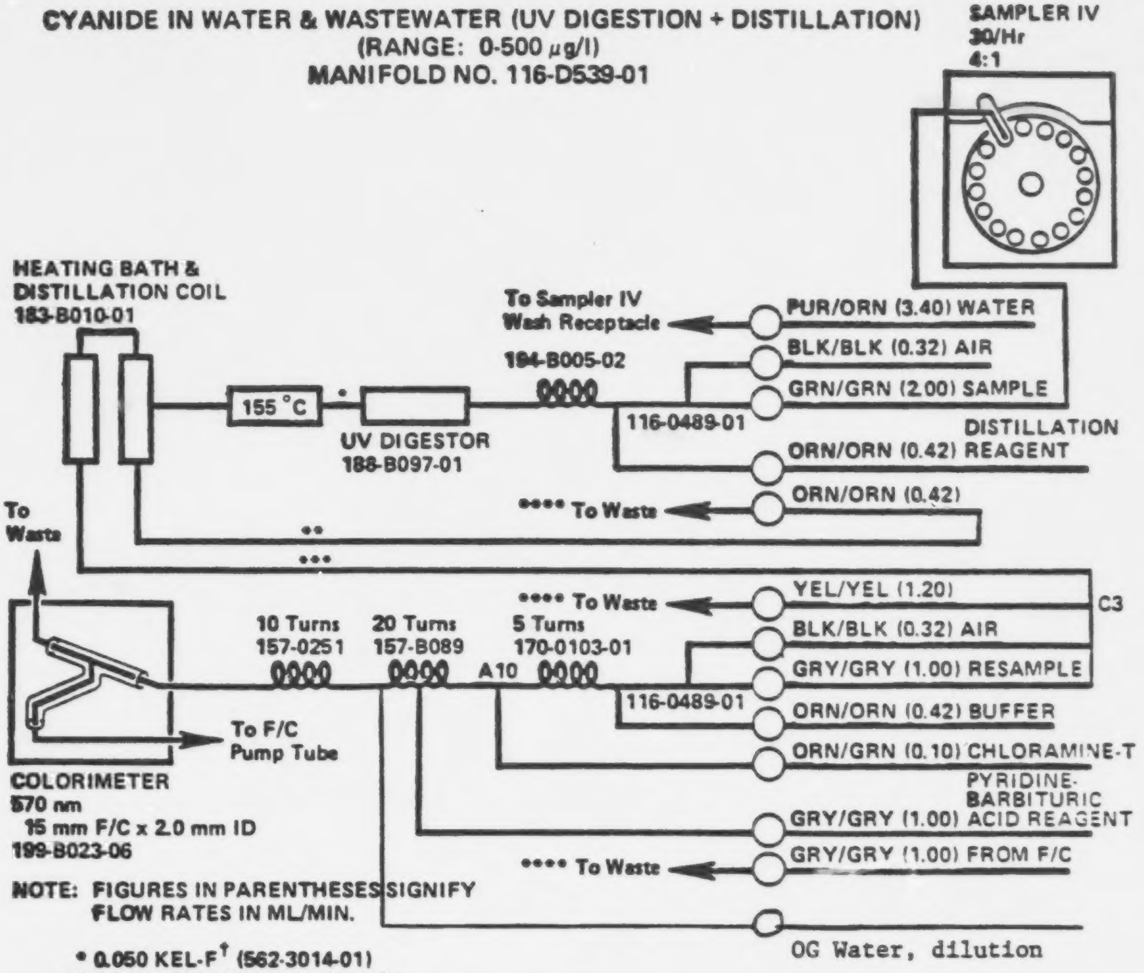
Calculations

mg/l CN^-= Value read of the printer x dilution factor (if any)

Reference

1. Industrial Method No. 315-74W", Technicon Industrial Systems, Tarrytown, NY, August 1974.

CYANIDE IN WATER & WASTEWATER (UV DIGESTION + DISTILLATION)
(RANGE: 0-500 µg/l)
MANIFOLD NO. 116-D539-01


SAMPLER IV
30/Hr
4:1
HEATING BATH &
DISTILLATION COIL
183-B010-01
To Sampler IV
Wash Receptacle
PUR/ORN (3.40) WATER
BLK/BLK (0.32) AIR
194-B005-02
GRN/GRN (2.00) SAMPLE
155 °C
*
UV DIGESTOR
188-B097-01
116-0489-01
DISTILLATION
ORN/ORN (0.42) REAGENT
**** To Waste
ORN/ORN (0.42)
To
Waste
**
***
**** To Waste
YEL/YEL (1.20)
C3
10 Turns
157-0251
20 Turns
157-B089
5 Turns
170-0103-01
BLK/BLK (0.32) AIR
A10
GRY/GRY (1.00) RESAMPLE
116-0489-01
ORN/ORN (0.42) BUFFER
To F/C
Pump Tube
ORN/GRN (0.10) CHLORAMINE-T
PYRIDINE-
BARBITURIC
GRY/GRY (1.00) ACID REAGENT
COLORIMETER
570 nm
15 mm F/C x 2.0 mm ID
199-B023-06
**** To Waste
GRY/GRY (1.00) FROM F/C
OG Water, dilution

NOTE: FIGURES IN PARENTHESES SIGNIFY FLOW RATES IN ML/MIN.

* 0.050 KEL-F† (562-3014-01)
** 0.100 ACIDFLEX (116-0538-17)
*** 0.034 POLYETHYLENE (562-2004-01)
**** SEE OPERATING NOTE 8.

†TRADEMARK OF 3-M COMPANY.

Determination of Ammonia-Nitrogen in Sediments and Other Solids
CRL Method No. 324

Scope and Application

This procedure is applicable to those ammonia compounds which are readily leachable from sediments and other solids.

Summary of Method

Five ml of 20% sulfuric acid are added to 2 grams of wet sample. Following standing and the addition of water, the sample is homogenized, settled and stored at 4°C overnight and a portion is pipetted out for analysis using the automated colorimetric phenate method for ammonia-nitrogen (CRL method # 312). Alkaline phenol and hypochlorite react with ammonia in the presence of sodium nitroprusside to form indophenol blue. The intensity of the blue color is proportional to the concentration of ammonia.

Equipment

Mettler PR 700 balance
360 ml high density polyethylene bottles
Self-sticking labels (yellow)
Tekmar SDT homogenizer
Technicon AA II system (see CRL Method # 312, Attached)

Reagents

Twenty percent H_2SO_4 . See CRL Method # 312, Attached)

Procedure

1. Place self-sticking labels on the sample bottles and write the sample numbers and date prepared. Label one bottle "blank" and date it.

2. Tare a polyethylene bottle on the PR 700 balance.

3. Weigh 1.5 to 2.0 g of homogenized bottom sediment directly into the bottle. Weigh out the larger amount for sandy samples, the lesser amount for samples with large amounts of humic material.

4. Record the weight of the sample on the bottle label.

5. Add 5 ml of the 20% H_2SO_4 solution to the yellow labeled bottle.

6. Shake the sediment-preservative mixture and let stand for 5 minutes, add 245 ml of distilled-deionized water to each bottle and shake.

7. Homogenize all samples with the Tekmar SDT instrument for 1 minute at high speed. Rinse the shaft and generator between samples with distilled-deionized water and wipe dry with a Kim-Wipe.

8. Store the sulfuric acid-preservated samples at 4°C overnight (but not longer than 24 hours if possible).

9. Fill the autoanalyzer sampling cup with each sample using an Eppendorf pipet (usually 7-10 ml or a dilution of the sample).

10. Proceed with ammonia analysis using CRL Method # 312 (Attached).

Quality Control

Prepare every tenth sample in duplicate or one duplicate per sample set if the set contains less than 15 samples.

Prepare a reagent blank for the H_2SO_4 preservative every day samples are prepared.

The PR 700 balance is set at zero and re-calibrated for each weighing.

Calculations

$$\text{mg/kg (dry) } NH_3 = \frac{\text{mg/l from AA} \times 1000 \text{ g/kg}}{\text{g/l (dry wt)}}$$

dry wt (g/l) = % solids(decimal fraction)x wet wt. x 4 (if 250 ml orig. volume was used)

References

1. Methods of Soil Analysis, ASA Monograph No. 9 part 2, 1965, "Inorganic Forms of Nitrogen" by J.M. Bremner, Chapter 84, pp. 1179-1206.

2. "EPA Methods for Chemical Analysis of Water and Wastes", 1974, Office of Technology Transfer, Wash., D.C., pp. 168-171.

Ammonia Nitrogen
(Automated Colorimetric Phenate Method)
CRL Method No. 312

Scope and Application

This method is applicable to surface and waste waters. The range is from 0.03 to 10.00 mg/l NH_3-N. Forty samples can be analyzed per hour.

Summary of Method

Alkaline phenol and hypochlorite react with ammonia in the presence of sodium nitroprusside to form indophenol blue. The intensity of the blue color is proportional to the concentration of ammonia.

Sample Handling and Preservation

Samples are collected in polyethylene bottles, and are preserved with 1 ml H_2SO_4 per liter of sample. Reagent blanks of 1 ml H_2SO_4 per liter of distilled water are collected and analyzed with the samples.

Interferences

The complexing reagent of potassium sodium tartrate plus sodium citrate prevent the precipitation of alkaline earth and heavy metals from occurring.

The pH of the final solution must maintained between 11.4 and 11.6. This method compensates for the acid used for preservation.

Sample turbidity may interfere. These samples can be decanted or filtered prior to analysis.

Colored samples which absorb at 630 nm result in a positive interference.

Metal ions in concentration up to 100 mg/l do not significantly interfere.

Nitroprusside is present to stabilize the formation of indophenol blue and avoid an irregular response in samples containing heavy metals.

Equipment

Technicon AA II system consisting of:

Sampler IV
Proportioning Pump II
Manifold with 1/5 dilution loop and 55°C internal heating bath
Colorimeter with 15 mm flowcell and 630 nm filters.
Recorder
Digital Printer

Reagents

Distilled water: NH_3 - free. All reagents must be made with NH_3-free water.

Wash water: Add 1 ml. H_2SO_4 to 1 liter distilled water.

Sulfuric acid (5N): Air scrubber solution. Carefully add 139 ml of conc. H_2SO_4 to about 500 ml of distilled water. Cool and dilute to 1 liter with distilled water.

Sodium phenolate: In a 1 liter beaker containing about 500 ml distilled water dissolve 83 g phenol and 36 g NaOH. Transfer the solution to a liter volumetric flask. Cool and dilute to 1 liter.

Sodium hypochlorite solution: Dilute 200 ml of a bleach solution containing 5.25% available chlorine (eg. Clorox) to 1 liter with distilled water.

Complexing reagent: Dissolve 33 g of potassium sodium tartrate and 24 g of sodium citrate in about 500 ml of distilled water. Add 7.6 ml of 10% NaOH solution and dilute to 1 liter. Add 0.25 ml Brij.-35.

Sodium nitroprusside: Dissolve 0.5 g of sodium nitroprusside in 500 ml of distilled water and dilute to 1 liter.

Stock standard solution A: Dissolve 3.819 g of anhydrous ammonium chloride, dried at 105°C, in distilled water. Add 1 ml of H_2SO_4 and dilute to 1 liter 1.0 ml = 1.0 mg NH_3-N.

Stock standard solution B - Add 1 ml of H_2SO_4 to 100 ml stock standard solution A. Dilute to 1 liter. 1 ml = 0.1 mg NH_3-N.

Working standard solutions. Prepare the following standards by diluting suitable volumes of stock standard solution A to 1 liter with distilled water. (One ml H_2SO_4 must also be added):

NH_3-N mg/l	ml std soln. B/l
3.00	3.00
5.00	5.00
10.00	10.00

Procedure

Set up manifold as in fig. 1. Allow the colorimeter, recorder, and printer to warm up for at least 15 minutes. Synchronize the spans of the 3 instruments with a range of 0.00 to 10.00 on the printer. A stable baseline should be obtained with all reagents in about 15 min.

Arrange standards and samples in the sampler tray. To avoid contamination, an Oxford pipet with disposable tips should be used to dispense samples. The following pattern is suggested for use without the computer:

5.0 std
5.0 std
10.0 std
10.0 std
3.0 std
3.0 std
BLK (1 ml H_2SO4/l dist. H_2O
BLK
Control std A.
Control std B.
BLK
- 39. samples and sample blanks (A blank always precedes a sample blank)
40. Duplicate of a sample around position 20

Note: Calibration standards are used in the first wheel only. Control standards, blanks, and duplicates are used in every wheel.

Turn on sampler and begin analysis. Only the standards in the first wheel are used to calibrate the instrument.

Quality Control

The concentrations of the control standards and the second of each pair of blanks are recorded in the AQC book. The duplicate values and standard cal. reading are recorded.

If more than one item of quality control data falls outside of the set control limits (usually +3 standard deviations), the data for that wheel must be discarded.

When running without the computer, the baseline may be reset during the run when a pair of blanks is analyzed. However, only minor adjustments should be made.

Control limits:

blank	0-0.03 mg/l
Control A	3.88-4.12 mg/l
Control B	4.88-5.12 mg/l
Difference in duplicates	0.03 mg/l or 3%

Calculations

The NH_3-N concentration is obtained directly from the Digital Printer in mg/l.

References

1. Methods for Cehmical Analysis of Water and Wastes, (1974), p. 168.

2. Technicon Industrial Method No. 154-71W/Tentative (1971).

Modification for Low Level Ammonia
CRL Method No. 315

Scope and Application

This method is applicable to surface and lake waters. The range is from 0.003 to 1.000 mg/l NH_3-N. Forty samples can be analyzed per hour.

Equipment

Technicon AA II system consisting of:

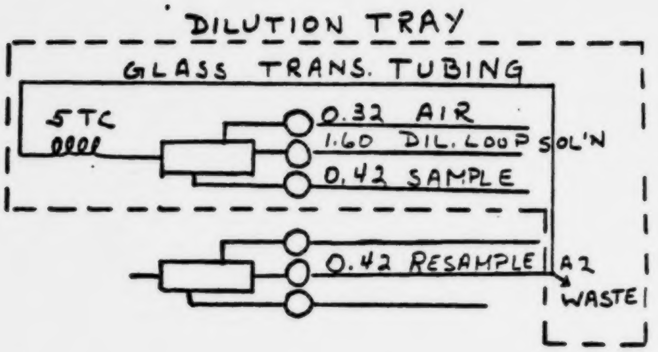
Sampler IV
Proportioning Pump III
Manifold with internal heating bath
(Bypass the dilution loop.)
Colorimeter with 15 mm. flowcell and 630 nm filters.
Recorder
Digital Printer

Reagents

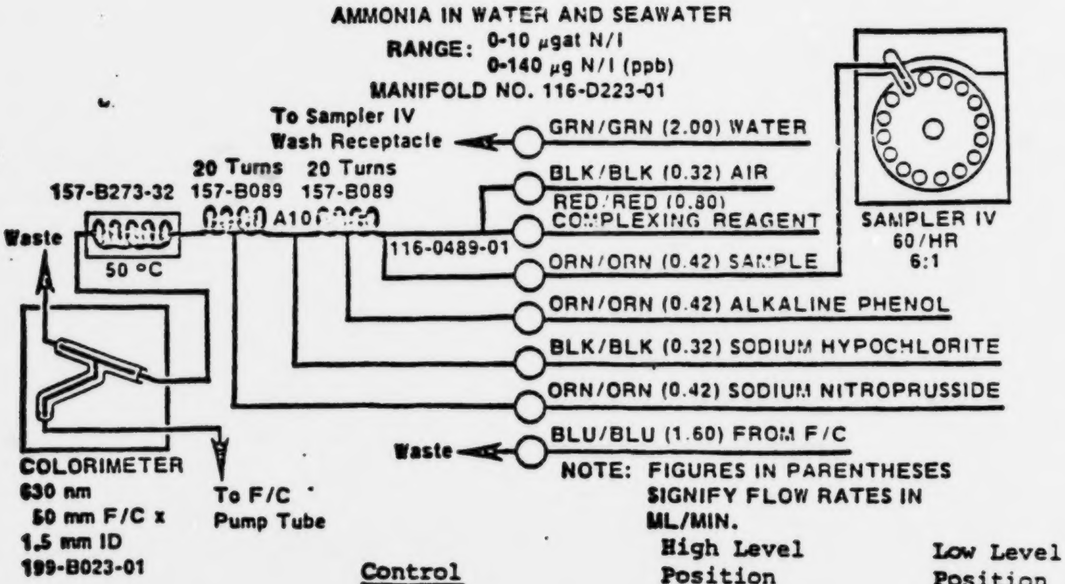
Working standard solutions: Prepare the following standards by diluting suitable volumes of stock standard solution B to 1 liter with distilled water. (One ml H_2SO_4 must also be added.):

NH_3-N mg/l	ml std. sol'n B/l
0.2	2.0
0.6	6.0
1.0	10.0

Figure 1.


DILUTION TRAY
GLASS TRANS. TUBING
5TC
0.32 AIR
1.60 DIL. LOOP SOL'N
0.42 SAMPLE
0.42 RESAMPLE
A2
WASTE

Use dilution loop
for high level only.


AMMONIA IN WATER AND SEAWATER
RANGE: 0-10 μgat N/l
0-140 μg N/l (ppb)
MANIFOLD NO. 116-D223-01
To Sampler IV
Wash Receptacle
GRN/GRN (2.00) WATER
BLK/BLK (0.32) AIR
RED/RED (0.80)
COMPLEXING REAGENT
ORN/ORN (0.42) SAMPLE
ORN/ORN (0.42) ALKALINE PHENOL
BLK/BLK (0.32) SODIUM HYPOCHLORITE
ORN/ORN (0.42) SODIUM NITROPRUSSIDE
BLU/BLU (1.60) FROM F/C
Waste
SAMPLER IV
60/HR
6:1
20 Turns
157-B089
20 Turns
157-B089
157-B273-32
A10
116-0489-01
Waste
50 °C
COLORIMETER
630 nm
50 mm F/C x
1.5 mm ID
199-B023-01
To F/C
Pump Tube

NOTE: FIGURES IN PARENTHESES SIGNIFY FLOW RATES IN ML/MIN.

Control	High Level Position	Low Level Position
Mode	normal	normal
Sampling Rate	40	40
Range	1000	1000
Decimal	0.00	000

2

Determination of Total Kjeldahl Nitrogen in
Sediments and Other Solids
CRL Method No. 468

Scope and Application

This method is applicable to the determination of TKN from nitrogen components of sediments such as amino acids, proteins and peptides which are converted to ammonia by strong acid-catalyzed digestion. Some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines may not be converted to ammonia, hence low TKN values will result.

Summary of Method

The homogenized sample is digested with a concentrated solution of sulfuric acid-potassium sulfate-mercuric oxide, to SO_3 fumes and until the solution becomes colorless or pale yellow. The residue is cooled diluted to volume, centrifuged and analyzed by the automated colorimetric method for ammonia-nitrogen (CRL Method No. 312). Alkaline phenol and hypochlorite react with ammonia in the presence of sodium nitroprusside to form indophenol blue. The intensity of the blue color is proportional to the concentration of Ammonia.

Equipment

Mettler PR 700 Balance
Pyrex test tubes (1" x 8" heavy walled, See CRL Method 465, Attached)
360 ml high density polyethylene bottles
Self-sticking labels (yellow)
Tekmar SDT homogenizer
Technicon AA II system (See CRL Method 465, Attached)
Automatic pipetter

Reagents

20% H_2SO_4 Solution.

Digestion Solution: Dissolve 2.0 grams of HgO in 25 ml of 6N H_2SO_4. In a separate beaker, add 200 ml of concentrated H_2SO_4 carefully to 500 ml of water. Then add 134 grams of potassium sulfate to the hot solution. After the potassium sulfate has dissolved add the HgO solution, cool and dilute to one liter. Store above 20°C.

Other Reagents (See CRL Method 465, Attached)

Procedure

1. Place self-sticking labels on the sample bottles and write the sample number and date prepared. Label one bottle for the reagent blank and one for duplicates; date the bottles.

2. Tare each polyethylene bottle on the PR 700 balance.

3. Weigh 1.5 to 3.0 grams of homogenized sediment directly into the bottle. Weigh the larger amount for sandy samples, the least amount for samples with large amounts of humic material.

4. Record the weight of the sample on the bottle label and lab sheet.

5. Add 5 ml of the 20% H_2SO_4 to sample in the yellow labeled bottle.

6. Shake the mixture, let stand for 5 minutes then add 245 ml of distilled-deionized water to each bottle and shake.

7. Blend (homogenize) for 1 minute at high speed. Sandy samples require less time, mud samples more time. Rinse the shaft and generator between samples with distilled-deionized water and wipe dry with a Kim-Wipe or other tissue.

8. Store the sulfuric acid-preserved samples at 4°C.

9. In a test tube rack, place 3 teflon boiling chips (which were acid rinsed in 1:1 HCl) into each clean, empty 1" x 8" test tube.

10. Reblend the sample in the bottle. Take a representative aliquot usually 10 ml or less (or as determined from ammonia analysis values. Generally if ammonia was high, TKN will also be high) and pipet into the tube containing boiling chips. Dilutions should be made with a blank solution which contains 2 ml of concentrated H_2SO_4 per liter of water. If the pen goes off scale, a smaller sample must be taken.

11. To each sample tube, pipet 2 ml of digestion solution.

12. Put each tube in the Technicon BD40, Block Digestor at low temperatude (200°C) and digest samples for a minimum or 1 hour or until all liquid has evaporated.

13. Transfer to the high temperature block digester and digest at 370°C while sulfur trioxide (SO_3) fumes are being emitted. After SO_3 evolution has stopped, digest for 30 to 40 minutes more at 370°C.

14. Cool for approximately 5 to 7 minutes (not longer, otherwise, a solid, insoluble, hard mass will result).

15. Add 10 ml of distilled-deionized water to each tube and cover the rack with foil.

16. Proceed with analysis using the manifold in CRL Method No. 465, Attached).

Quality Control

One field reagent blank containing preservative and digestion solution and one duplicate are analyzed for each group of samples. If twenty or more samples are analyzed two blanks and duplicates are analyzed.

The autoanalyzer is calibrated according to the manufacturers specifications.

The PR 700 balance is set zero and recalibrated for each weighing.

Calculations

$$\text{ug/kg (dry) TKN} = \frac{\text{mg/l from method 465 curve x 1000 g/kg}}{\text{g/l (dry wt. of original sample)}}$$

$$\text{dry wt. (g/l)} = \text{\% solids (decimal fraction) x wet wt. x } \frac{1000}{250} \text{ (orig. volume).}$$

References

1. "EPA Methods for Chemical Analysis of Water and Wastes", 1974, Office of Technology Transfer, Washington, DC, p. 175-181.

2. "Ultramicro Semi-Automated Method For the Simultaneous Determination of Total Phosphorus and Total Kjeldahl Nitrogen in Wastewaters", Jirka, A.M., Carter, M.J., May, D., and Fuller, F.D., Environmental Science and Technology Vol. 10, 1976, p. 1038-1043.

Determination of Total Kjeldahl (TKN) Nitrogen and Total Phosphorus (TP) in Water and Wastewater
CRL Method #465

Scope and application

This method is an ultramicrotechnique for the digestion of organic nitrogen and phosphorus compounds in a variety of wastewater samples. The digest is analyzed simultaneously for phosphate and ammonia in the range of 0.2 - 4.0 mg/l and 0005 - 10 mg/l at a rate of 30 samples per hour.

Summary of Method

The samples are digested with sulfuric acid containing potassium sulfate and mercuric oxide as catalyst. Then, in heavy walled pyrex tubes, the tubes are heated in a technicon BD-40 Block digestor. The digested samples are then automatically analyzed for TKN and TP using the Technicon AA II system.

Equipment

Technicon BD-40-Block digestor.

Technicon Autoanalyzer II consisting of

Sampler IV with 30/hour 2:1 cam, proportionating pump III with a dilution manifold.

Phosphate manifold

Ammonia manifold

Colorimeter equipped with 15 mm flow cell, S10 phototube, 630 nm interference filter for TKN.

Colorimeter equipped with 50 mm flow cell, S_1 phototube and 880 nm interference filters for TP.

Dual pen recorder

Dual channel digital printer

Tekmar Model SDT homogenizer

Oxford 5-10 ml adjustable pipett

Teflon boiling chips

Vortex genic mixer

Precision vari-hi speed centricore centrifuge

Reagents

All chemicals are ACS reagent grades

Digestion Solution: Dissolve 2.0 gm of HgO in 25 ml of 6N H_2SO_4.

Add 200 ml of conc. H_2SO_4 carefully to 500 ml water. While the strong acid solution is still Hot, 134 gm of K_2SO_4 was dissolved in it. Add the HgO solution to sulfuric acid - sulfate solution, allow to cool and dilute to one liter, and store above 20°C to avoid precipitation of K_2SO_4.

Reagents for automated dilution manifold: sample wash solution

Add 35 ml of conc. H_2SO_4 to 500 ml of H_2O and dilute to 1 liter with distilled water.

Dilution Solution: Dilute 12.5 ml of 10 N NaOH to 1 liter with distilled water.

Reagents for automated ammonia manifold: Complexing reagent:

Dissolve 33 gm of sodium tartrate, 24 gm of sodium citrate in 900 ml of distilled water, and dilute 1 liter and add 0.25 ml of Brig 35 wetting agent.

Alkaline Phenol Solution: Dissolve 83 gm of Phenol and 36 gm of NaOH in 900 ml of distilled water, dilute to one liter. Store at 4°C.

Sodium Hypochlorite Solution: Dilute 200 ml of "Chlorox" to 1 liter with distilled water.

Sodium nitropusside reagent: Dissolve 0.5 gm of sodium nitroprusside in 900 ml of water and dilute to 1 liter. Store at 4°C.

Reagents for Automated Phosphate Manifold
Sodium Chloride Solution: Dissolve 5 gm of sodium chloride in 900 ml of distilled water, dilute to one liter. Add 0.25 ml of Levor IV wetting agent.

4.9N Sulfuric Acid: Add 136 ml of conc H_2SO_4 to 500 ml of distilled water, cool and dilute to one liter.

Ammonium Molybdate Solution: Dissolve 40 gm of $(NH_4)_6\ MO_7O_{24}\ 4H_2O$ in 900 ml of distilled water and dilute to one liter.

Store at 4°C.

Ascorbic acid solution: Dissolve 18 gm of ascorbic acid in 900 ml of water and dilute to one liter. Store at 4°C.

Antimony Potassium Tartrate: Dissolve 3.0 gm of K(SbO) $C_4H_4O_6.1/2\ H_2O$ in 900 ml of distilled water and dilute to 1 liter. Store at 4°C.

Combined Color Reagents for TP

Add 15 ml of Amm. Molybdate solution to 30 ml of ascorbic acid solution then add 5 ml of antimony potassium tartrate. This reagent has to be prepared fresh before each run.

Standards: Stock nitrogen standard [0.1 mgN/ml]: Dissolve 1.05 gm of glutamic acid [dried at 105°C for one hour] and in 900 ml of distilled water, add 2 ml of conc H_2SO_4 and dilute to one liter.

Stock phosphorus standard [0.1 mgP/ml]
Dissolve 0.4394 gm of KH_2PO_4 [dried at 105°C for one hour], in 900 ml of distilled water, add 2 ml conc. H_2SO_4 and dilute to 1 liter.

Combined Standards: Prepare the following standards

	ml P. Stock	ml N. Stock
0.4 mg P/l + 2.00 mgN/l	4	20
2.00 mg P/l + 5.00 mgN/l	20	50
4.00 mg P/l + 10.00 mgN/l	40	100

Dilute each combination to one liter [add 1 ml conc. H_2SO_4 for preservation before diluting to one liter].

Blank Solution: Add 1 ml of H_2SO_4 to 900 ml of distilled water and dilute to one liter.

Procedure

1. All glassware should be rinsed with 1:1 HCl to prevent phosphorous contamination. Rinse the digestion tubes with hot water followed by 1:1 HCl and finally with distilled water. The tubes should be rinsed immediately after usage with hot water to prevent hardening of any deposits.

2. Follow this loading pattern in filling the tubes in the rack: set standard, followed by 3 blanks, 3 calibration standards, 2 control standards, field blanks, samples then finally a duplicate at position 40.

3. Any non-uniform samples such as sewage, paper mill waste, farm wastes etc., should be blended for 30 seconds and aliquots withdrawn immediatly after blending.

4. Fill the rack with the digestion tubes.

5. Add a few teflon boiling chips or stones.

6. A representative 10 ml aliquot of standards, blanks, Q.C. standards and samples is delivered to the digestion tubes using the Oxford pipette with the disposable tips. Follow the loading pattern discribed in 2 above.

7. Add 2 ml of digestion mixture to each tube.

8. Place the rack of tubes in Block Digestor A [adjusted to 200°C] for 1/2 hour to allow evaporation of the samples.

9. Transfer the rack of tubes to Block digestor B [adjusted to 370°C] for another 1/2 hour. The digestion should be complete by then.

10. Remove the rack and allow the tubes to cool to room temp.

11. Add 10 ml of distilled water to each tube and mix the sample with the vortex mixer. Centifuge if necessary. Suspended, dark materials present after digestion indicate incomplete digestion and the sample should be discarded.

12. Transfer each sample to a clean 15 x 85 mm test tube and place in the technicon sample tray in the same loading pattern described.

13. Set up the manifold and reagents as shown in Figs. 1, 2, 3 and allow the colorimeter, recorder and printer to warm up.

14. Feed all reagents through the lines with the sample probe at the wash cycle.

15. Check the zero and full scale set on the colorimeter.

16. Switch to normal mode and adjust the baseline below the zero line on the recorder to faciliate zeroing the instrument later with the blanks.

17. Start the analysis. Synchronize the instrument with the set standard, then set the zero baseline with the 1st blank and calibrate the instrument with the 1st calibration standard [a midscale or a full scale standard could be used]. The instrument is recalibrated for every 40 sample set.

18. Samples following an off scale sample(s) should be rerun at the end of the wheel to correct for carryover effects.

Quality Control

A minimum of two duplicates, field reagent blanks, and 2 quality control standards are run with every 40 samples or set.

Calculations

The TP and TKN concentrations in mg/l are obtained directly from the digital printer, times any dilution factor if necessary.

References

Jirka, Andrea M., Carter, Mark J., May, Dorothy, and Fuller, Fredrick D., "Ultramicro-Semi-Automated Method For the Simultaneous Determination of Total Phosphorus and Total Kjeldahl Nitrogen in Wastewaters", Environmental Science and Technology, Volume 10, 1976, p. 1038-1043.

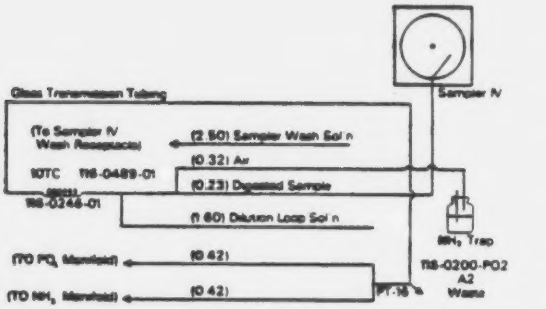

Sampler IV
Glass Transmission Tubing
(To Sampler IV Wash Receptacle)
(2.50) Sampler Wash Sol'n
(0.32) Air
10TC 116-0489-01
(0.23) Digested Sample
116-0246-01
(1.60) Dilution Loop Sol'n
NH$_3$ Trap
(TO PO$_4$ Manifold)
(0.42)
(TO NH$_3$ Manifold)
(0.42)
PT-16
116-0200-PO2
A2
Waste

Figure 1. Automated total phosphorus and total Kjeldahl nitrogen dilution manifold

Numbers in parentheses correspond to flow rate of pumptubes in ml/min. Numbers adjacent to glass coils and fittings are Technicon Corp. part numbers

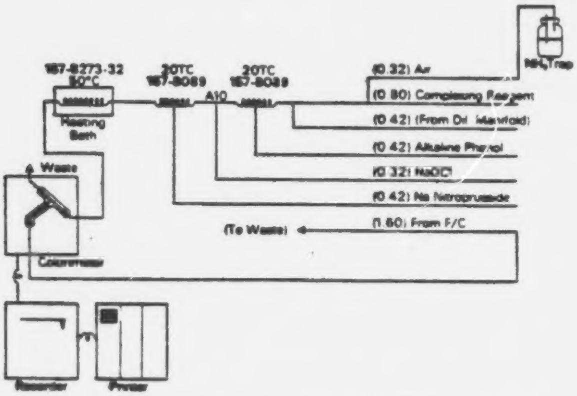

167-8273-32
50°C
Heating Bath
20TC
167-8089
A10
20TC
167-8089
NH$_3$ Trap
(0.32) Air
(0.80) Complexing Reagent
(0.42) (From Dil. Manifold)
(0.42) Alkaline Phenol
(0.32) NaOCl
(0.42) Na Nitroprusside
(To Waste)
(1.60) From F/C
Waste
Colorimeter
Recorder
Printer

Figure 2. Automated ammonia manifold, 0.06–10.00 mg N/l. For explanation of manifold numbers, see Figure 1

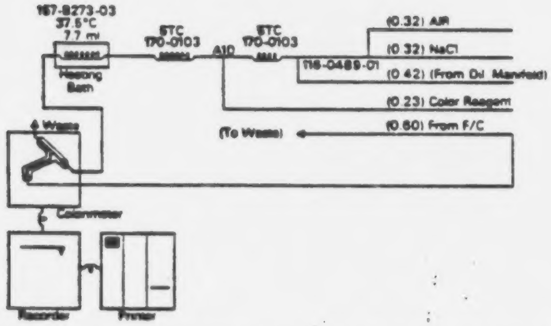

167-8273-03
37.5°C
7.7 ml
Heating Bath
5TC
170-0103
A10
5TC
170-0103
116-0489-01
(0.32) AIR
(0.32) NaCl
(0.42) (From Dil. Manifold)
(0.23) Color Reagent
(To Waste)
(0.60) From F/C
Waste
Colorimeter
Recorder
Printer

Figure 3. Automated phosphate manifold, 0.02–2.00 mg P/l. For explanation of manifold numbers, see Figure 1

Determination of Total Phosphorus in Sediments and Other Solids
CRL Method No. 435

Scope and Application

This method is applicable to the determination inorganic and organic phosphorus forms in sediment and other solid samples.

Summary of Method

The sample is digested with a strong sulfuric acid - potassium sulfate - mercuric oxide solution to sulfur trioxide fumes (SO_3) and for 30-40 minutes longer. The solution is cooled, diluted, and an aliquot analyzed by the automated molybdate reaction. Ammonium mobybdate and antimony potassiumtartrate react in an acid medium to form an antimony - phospho - molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

Equipment

Pyrex test tubes (1" x 8:", heavy walled) see CRL Method 465 - Attached to CRL Method 468.
Technicon AA II System (see CRL Method 465, Attached to CRL Method 468)
Automatic Pipetter
Mettler PR 700 Balance
360 ml high density polyethylene bottles
Self - Sticking labels (yellow)
Tekmar SDT homogenizer

Reagents

20% H_2SO_4 Solution.
Digestion Solution: Dissolve 2.0 grams of Hgo in 25 ml of 6N H_2SO_4. In a separate beaker, add 200 ml of concentrated H_2SO_4 carefully to 500 ml of water. Then add 134 grams of potassium sulfate to the hot solution. After the potassium sulfate has dissolved add the HgO solution, cool and dilute to one liter. Store above 20°C.

Other Reagents (See CRL Method 465, Attached to CRL Method 468)

Procedure

1. Place self-sticking labels on the sample bottles and write the sample numbers and date prepared. Label one bottle for the reagent blank and one for duplicate. Date the bottles.

2. Tare each polyethylene bottle on the PR 700 balance.

3. Weigh 1.5 to 3.0 grams of homogenized sediment directly into the bottle. Weigh the larger amount for sandy samples, the lesser amount for samples with large amounts of humic material.

4. Record the weight of the sample on the bottle label and lab sheet.

5. Add 5 ml of the 20% H_2SO_4 to sample in the yellow labeled bottle.

6. Shake the mixture, let stand for five minutes then, add 245 ml of distilled-deionized water to each bottle and shake.

7. Blend (homogenize) for one minute at high speed. Sandy samples require less time, mud samples more time. Rinse the shaft and generator between samples with distilled-deionized water and wipe dry with a Kim-Wipe or other tissue.

8. Store the sulfuric acid-preserved samples at 4°C.

9. In a test tube rack, place three teflon boiling chips (which were acid rinsed with 1:1 HCl) into each clean, empty 1" x 8" test tube.

10. Reblend the sample in the bottle. Take a representative aliquot, (usually 10 ml for colorimetric analysis. If an aliquot smaller than 10 ml is taken, dilutens should be made with a blank solution which contains 2 ml of concentrated H_2SO_4 per liter of water.

11. To each sample tube, pipet 2 ml of digestion solution.

12. Put each tube in the Technicon BD40 Block Digestor at low temperatude (200°C) and digest samples for a minimum or one hour or until all liquid has evaporated.

13. Transfer to the high temperature block digester and digest the samples at 370°C while sulfur trioxide (SO_3) fumes are being emitted. After SO_3 evolution has stopped, digest for 30 to 40 minutes more at 370°C.

14. Cool for approximately five to seven minutes (not longer, otherwise a solid, insoluble, hard mass will result).

15. Add 10 ml of distilled-deionized water to each tube and cover rack with foil or other cover.

16. Proceed with analysis using the manifold in CRL Method No. 465, (Attached to CRL Method 468).

Quality Control

One field reagent blank containing preservative and digestion solution and one duplicate are analyzed for each group of samples. If twenty or more samples are analyzed, two blanks and duplicates are analyzed.

The autoanalyzer is calibrated according to the manufacturer's specifications

The PR 700 balance is set to zero and recalibrated for each weighing.

Calculations

$$\text{mg/kg (dry) Total P} = \frac{\text{mg/l from Method 465 curve x 1000 g/kg}}{\text{(g/l (dry wt. of original sample)}}$$

$$\text{dry wt. (g/l)} = \text{\% solids (decimal fraction) x wet wt. x } \frac{1000}{250} \text{ (orig. volume)}$$

References

1. "EPA Methods for Chemical Analysis of Water and Wastes", 1974, Office of Technology Transfer, Washington, DC, p. 249-255.

2. "Ultramicro Semi-Automated Method For the Simultaneous Determination of Total Phosphorus and Total Kjeldahl Nitrogen is Wastewaters", Jirka, A.M., Carter, M.J., May, D., and Fuller, F.D., Environmental Science and Technology, Vol. 10, October 1976, p. 1038-1043.

Determination of Chemical Oxygen
Demand in Sediments and Other Solids
CRL Method No. 351

Scope and Application

This method is applicable to sediments and other solids. It is a measure of the quantity of oxygen required to oxidize organic matter in sediments and solids under specific conditions of oxidizing agent, temperature and time.

Summary of Method

Organic substances in the sample are oxidized by potassium dichromate in 50% sulfuric solution at reflux temperature. Silver sulfate is used as a catalyst and mercuric sulfate is added to remove chloride interference. Following digestion, an automated spectrophotometric measurement of the appearance of chromium III at 600 nm is used to determine the Chemical Oxygen Demand (COD) of the sample.

Equipment

Screw cap, teflon-lined culture test tubes (See CRL Method No. 342, Attached).
Technicon AA II System with Sample IV, and Pump III (See CRL Method 342, Attached).

Oven

Reagents

20% Sulfuric Acid

Digestion Solution - Dissolve 10.2169 of $K_2Cr_2O_7$, 167 ml of conc. $H_2SO_4$and 33.3 g of $HgSO_4$ in 500 ml of water and dilute to 1 liter.

Catalyst Solution - Dissolve 22 g of Ag_2SO_4 in a 9 lb. bottle of H_2SO_4.

Other Reagents - See CRL Method 342, Attached).

Procedure

1. Place self-sticking labels on the sample bottles and write the sample numbers and date prepared. Label one bottle for the reagent blank and one for duplicates; date the bottles.

2. Tare each polyethylene bottle on the PR700 balance.

3. Weigh 1.5 to 3.0 grams of homogenized sediment directly into the bottle. Weigh the larger amount for sandy samples, the lesser amount for samples with large amounts of humic material.

4. Record the weight of the sample on the bottle label and lab sheet.

5. Add 5 ml of the 20% H_2SO_4 to sample in the yellow labeled bottle.

6. Shake the mixture, let stand for 5 minutes then add 245 ml of distilled-deionized water to each bottle and shake.

7. Blend (homogenize) for 1 minute at high speed. Sandy samples require less time, mud samples more times. Rinse the shaft and generator between samples with distilled-deionized water and wipe dry with a Kim-Wipe or other tissue.

8. Store the sulfuric acid-preserved samples at 4°C.

9. Wash all of the culture tubes and caps with 20% H_2SO_4 to prevent contamination.

10. Shake the sample which was stored in the bottle and withdraw 2.5 ml of sample into the culture tube.

11. Add 1.5 ml of digestion solution and 3.5 ml of catalyst solution carefully down the side of the tube so that the acid forms a layer on the bottom of the tube.

12. Cap tightly and mix by shaking.

13. Prepare blanks and standards of KHP in the same manner (See CRL Method 342, Attached).

14. Heat in an oven for 2 hours at 150°C (making sure that the sample is refluxing).

15. Cool, remove from the oven and place in the Technicon Autoanalyzer sampling tray.

16. Proceed with the colorimetric analysis using the manifold shown in CRL Method 342, (Attached).

Quality Control

One field reagent blank (which includes 5 ml of 20% H_2SO_4 diluted to 250 ml) and a duplicate of one of the samples are analyzed for each group of samples. If twenty or more samples are analyzed, a minimun of two duplicates are analyzed.

Calculations

$$\text{mg/kg (dry) COD} = \frac{\text{mg/l COD from CRL Method 342} \times \text{1000 g/kg}}{\text{orig. wt of sample in grams per liter}}$$

$$\text{dry wt.} = \text{(g/l)} = \text{decimal fraction of \% solids} \times \text{wet wt.} \times \frac{1000}{250}$$

Reference

1. "Micro Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand", Jirka, Andrea M., Carter, Mark J., *Analytical Chemistry*, Vol. 47, July 1975, p. 1397.

Determination of Chemical Oxygen Demand in Water and Wastewater
CRL Method #342

Scope and Application

This method is applicable to waste water, lake water, drinking water, industrial wastes, raw and finished sewage.

Summary of Method

The semiautomated procedure for the determination of COD combines a micro sample digestion technique with an automated procedure based on the spectrophotometric measurement of Cr^{+++} at 600 nm: The sample is combined with an acid potassium dichromate, Mercuric sulfate and an acid silver sulfate solution in a specially capped culture tube. It is then digested in a 150°C oven for two hours and the concentration of Cr^{+++} is measured at 600 nm in a 50 mm flow cell. The range is 3-900 mg/l COD.

Equipment

Technicon Autoanalyser II consisting of
  Sampler IV with 40 x 3/1 cam
  Proportionating pump IV with a dilution manifold

Recorder II
  Single channel digital printer corning No. 9949 16 x 100 mm. Screw cap (Cap No.No. 9989) Culture Tubes

  Tekmar Model SDT Homogenizer
  Oven

Reagents

Digestion solution: Add 10.216 gm of $K_2Cr_2O_7$, 167 ml of conc. H2S04 and 33.3 gm of HgS04 to 500 ml of water and dilute the cooled solution to 1 liter.

Catalyst Solution: Dissolve 22 gm of Ag2S04 in a 9-lb bottle of conc. H_2SO_4.

Sampler Wash Solution: 50% sulfuric acid by volume.

Standards: Dissolve 8.5 gm of a dried portion of NBS standard reference material (84h) in water and dilute to 1 liter. The strength of this solution is 10 gm/l. Working standards of 50, 200, 500, and 800 mg/l are prepared by taking the proper dilutions.

Procedure

1. Wash all culture tubes and screw caps with 20% H_2SO_4 before use.
2. Place 2.5 ml of sample, and 1.5 ml of digestion solution into tubes.
3. Carefully add 3.5 ml of catalyst solution down the sides of the culture tube .
4. Cap the tube tightly and then shake to mix the contents.
5. Prepare five blanks, a set of standards and Quality Control Standards CS1, CS2 with each rack.
6. Heat all samples, blanks and standards in the oven at 150°C for two hours.
7. Set the analytical manifold and reagent as shown in Fig. (1) with a glass capillary as a sample probe.
8. Set the standard calibration control at 228.
9. Adjust the zero and full scale setting.
10. With all reagents passing through the lines and the sample probe in the wash cycle, turn the colorimeter to the proper damping and adjust the baseline below the zero line on the recorder.
11. Start the analysis and with the blanks, zero the baseline.
12. Check the preset - calibration (std. cal. at 228) and slightly adjust if needed with the 500 mg/l standard.

Quality Control

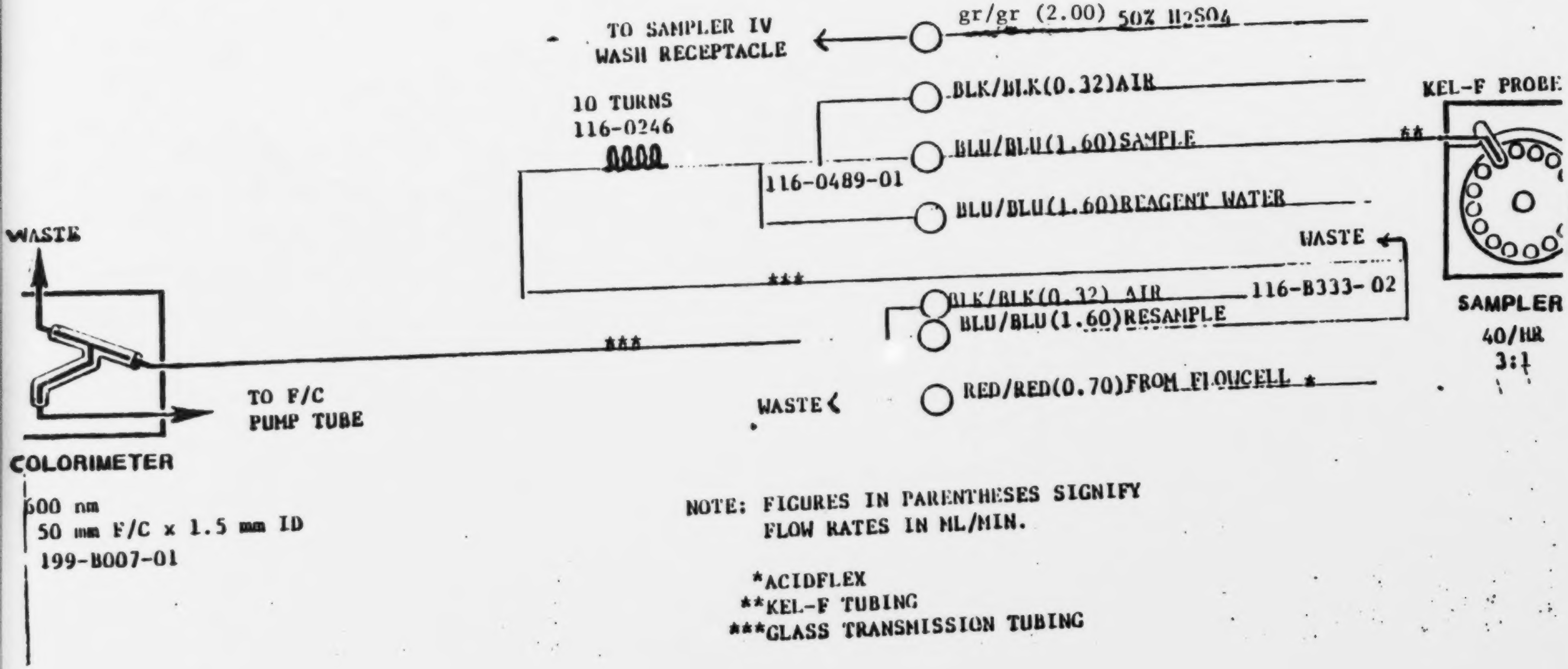
One field reagent blank and a duplicate of one of the samples is analyzed with each group of samples. If twenty or more samples are analyzed, a minimum of two blanks and two duplicates are analyzed.

Calculations

The COD values of the unknown samples are obtained by direct printout in mg/l times any dilution factor applicable.

References

"Micro Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand", Jirka, Andrea M., Carter, Mark J., Analytical Chemistry, Vol. 47, No. 8, July 1975, p. 1397.


TO SAMPLER IV
WASH RECEPTACLE
gr/gr (2.00) 50% H2SO4
BLK/BLK(0.32)AIR
BLU/BLU(1.60)SAMPLE
BLU/BLU(1.60)REAGENT WATER
10 TURNS
116-0246
116-0489-01
KEL-F PROBE
**
WASTE
***
BLK/BLK(0.32) AIR
116-B333-02
BLU/BLU(1.60)RESAMPLE
RED/RED(0.70)FROM FLOWCELL *
WASTE
***
WASTE
TO F/C
PUMP TUBE
COLORIMETER
600 nm
50 mm F/C x 1.5 mm ID
199-B007-01
SAMPLER
40/HR
3:1

NOTE: FIGURES IN PARENTHESES SIGNIFY FLOW RATES IN ML/MIN.

*ACIDFLEX
**KEL-F TUBING
***GLASS TRANSMISSION TUBING

Fig. 1 Manifold for Chemical Oxygen Demand

Determination of Total Mercury
in Sediments and Other Solids
CRL Method No. 393

Scope and Application

This method is applicable to the determination of inorganic and organic forms of mercury in sediments of virtually all types (clean, sandy, silty, clay, oozy, and organic-rich sludge) in the ranges from 0.1 mg/kg to 2 mg/kg (without dilution) and higher.

Summary of Method

Aqueous suspensions of homogenized sediment samples are automatically analyzed using the cold-vapor detection method following a persulfate oxidation and stannous chloride. Samples are analyzed at the rate of 30 per hour with a routine detection limit of 0.1 mgHg/kg of sample and an average relative standard deviation of 6% at a level of 20-30 mg/kg of mercury.

Equipment

Mettler PR700 Balance

360 ml high density polyethylene bottles

Self-Sticking labels

Tekmar SDT homogenizer

Pipets (wide tipped)

Mercury-free glassware (See CRL Method 390, Attached)

Spectro Products Mercury Analyzer With Perkin Elmer Model 56 Recorder (See CRL Method 390, Attached)

Technicon AA II System (See CRL Method 390, Attached)

Reagents

Preservative: To 500 ml of distilled water, add 250 ml of conc. HNO_3 and 25 g of potassium dichromate ($K_2Cr_2O_7$) and dilute to 1 liter.

1. Potassium Persulfate
2. Hydroxylamine Hydrochloride - Sodium Chloride
3. Stannous Chloride

In items 1, 2, and 3, see CRL Method 390 (Attached)

Procedure

1. Place self-sticking labels on the sample bottles and write the sample numbers and date prepared. Label reagent blank and duplicate sample bottles and date them.

2. Tare a polyethylene bottle on the PR 700 balance.

3. Weigh approximately 1.0 gram of homogenized sediment sample into the tared 360 ml polyethylene bottle. For sandy samples, slightly larger amounts may be used (1.5 to 2 grams). Larger sample sizes however often result in settling and clogging in the manifold. Pulverizing to a finer mesh allows usage of a larger sample size.

4. Record the weight of the sample on the bottle label.

5. Add 5 ml of preservative solution to the sample. If the $K_2Cr_2O_7$ is reduced, (as evidenced by a green color), add an additional amount of preservative solution until the suspension color remains yellow. Let stand for 5 minutes or until foaming subsides (usually sulfides and other gases are driven off).

6. If 5 ml of preservative was sufficient, add 245 ml of distilled-deionized water and homogenize at high speed for 1 minute, followed by manual shaking for another minute. If more than 5 ml of preservative are added, reduce the volume of distilled deionized water accordingly (final volume 250 ml is desired).

7. Rinse the shaft and generator between samples with distilled-deionized water and wipe dry with a kim-wipe tissue.

8. Store the sample overnight. (If a green color develops on standing, add more preservative to a yellow color and note the final volume).

9. Shake the sample and fill the autoanalyzer sampling cup. (Note-the autoanalyzer contains a cylindrical sterrer which keeps the sample in suspension).

10. Proceed with mercury analysis using CRL Method No. 390 (Attached).

Quality Control

One field reagent blank (which includes the H_2SO_4-$K_2Cr_2O_7$ preservative) and a duplicate of one of the samples are analyzed for each group of samples. If twenty or more samples are analyzed, a minimum of two duplicates are analyzed.

Calculations

$$\text{mgHg/kg (dry basis)} = \frac{\text{ugHg/l (from curve using Method 390) x 25}}{\text{(Orig. wt. in grams of sediment)x(decimal fraction of \% solids)}}$$

Reference

1. "An Automated Method for the Determination of Mercury in Sediments", Jirka, Andrea M. and Carter, Mark J., Analytical Chemistry, Vol. 50, January 1978, p. 91.

2. "Automated Method for the Determination of Total and Inorganic Mercury in Water and Wastewater Samples", EL-Awady, Miller and Carter, Analytical Chemistry, Vol. 48, No. 1, January 1976.

Total and Inorganic Mercury in
Water and Wastewater Samples
CRL Method No. 390

Scope and Application

This method is applicable to drinking water, wastewater, effluents, and a variety of environmental water matrices. Samples are analyzed at the rate of 20 per hour, with a routine detection limit of 0.1 ug/l and a working range of 0.1-2 ug/l.

Summary of Method

Samples are automatically analyzed using the cold-vapor detection method following a persulfate oxidation and stannous chloride reduction. The mercury vapor aerated from solution passes through a cell positioned in the light path of a spectrophotmeter mercury analyzer. Absorbance (peak heights) is measured as a function of mercury concentration.

Apparatus

Spectro products mercury analyzer, model HG-2.

Perkin Elmer model 56 multi-range chart recorder.

Harmonically smoothed voltage stabilizer.

Technicon Auto Analyzer unit consisting of
- a. Sampler IV
- b. Proportioning pump III
- c. Heating bath with heating coil (20 ft. long 2.4 mm id)

Absorption cell	Fig. 1
Gas liquid separator	Fig. 2

A rotameter to measure the rate of air flow in the gas liquid separator.

A Tekmar model SDT homogenizer.

Reagents

Preservative solution - add 250 ml of conc. HNO_3, 25 gm of $K_2Cr_2O_7$ to 500 ml

of distilled water and dilute to 1000 ml.

Sulfuric acid conc. - reagent grade, suitable for mercury determination.

Three percent hydroxylamine hydrochloride/hydrochloric acid reagent. Dissolve 30 gm of NaCl, 30 gm of hydroxylamine hydrochloride in one liter of distilled water.

Four percent potassium persulfate reagent. Dissolve 40 gm of $K_2S_2O_7$ salt in one liter of distilled water.

Stannous chloride/hydrochloric acid reagent. Add 225 ml of HCl to 500 ml of distilled water, add 10 gm of $SNCl_2$ and dilute to 1 liter.

Stock mercury solution - 1000 pm mercuric chloride ion methyl mercuric chloride could be used (reagent grade).

Working mercury standard. Prepare 0.1, 0.5, 1, 1.5, and 2 mg/l standards by taking the appropriate dilution of the 1000 mg/l stock solution.

Nitric acid was solution - add 100 ml of concentrated HNO_3 to 500 ml of distilled water and dilute to one liter.

Procedure

1. Set up manifold as in Fig. 3.

2. Feeding all the reagents through the system with acid wash solution through sample line, the vapor liquid separator disconnected, adjust heating bath to 150°.

3. Turn on the cooling water for the jacket mixer.

4. Adjust the nitrogen gas flow to 4 to 5 division on the scale.

5. Turn on the mercury analyzer and adjust the "B" lamp to read 100% full scale.

6. Allow 15-20 minutes for warm-up period and readjust the 100% scale for the "B" lamp.

7. Turn on the "Agc" if the meter deflects from the 100% reading, readjust using the "Agc" adjuster knob.

8. Balance the "B" lamp by increasing the power to the "A" lamp until 0% reading is obtained.

9. Turn on the 10X (scale expansion) and with the zero fine adjuster readjust the zero reading.

10. Turn on the recorder and monitor the baseline for 10 minutes or until a stable baseline is obtained.

11. Connect the gas separator to the absorption cell and monitor the baseline for 5 minutes.

12. Run 2, 1.0, 1, 0, 0.5, 0.1 ug/l standards, blanks. Prepare standard curve by plotting peak heights of processed standards against concentration values.

13. Analyze the samples and determine the mercury content from the standard curve.

14. After the analysis is completed, disconnect the gas separator and put all the lines in the washing solution, to wash out the system.

15. Turn off the recorder, the mercury analyzer and the nitrogen gas.

16. Turn off the autoanalyzer pump and remove the plate.

17. Unplug the heating bath.

18. Turn off the cooling water.

Quality Control

One field reagent blank (which includes the H_2SO_4-$K_2Cr_2O_7$ preservative, and a duplicate of one of the samples are analyzed for each group of samples. If twenty or more samples are analyzed a minimum of two duplicate are analyzed.

Calculations *

ug/l mercury = ug/l (from curve) x dilution factor (if any)

*A computer program is also used frequently for calculations. It involves calculations of the peak heights versus standard values using the best square fit.

Reference

"Automated Method for the Determination of Total and Inorganic Mercury in Water and Wastewater Samples", El-Awady, Miller and Carter, Analytical Chemistry, Vol. 48, No. 1, January 1976.

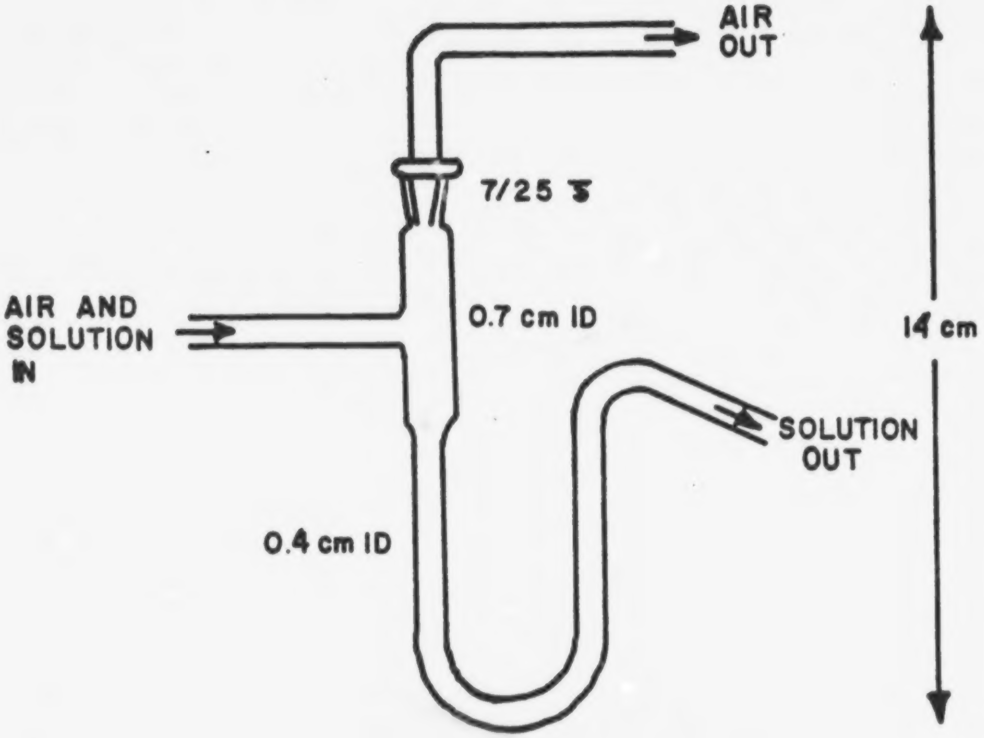

AIR OUT
7/25 $
AIR AND SOLUTION IN
0.7 cm ID
14 cm
SOLUTION OUT
0.4 cm ID

FIGURE 1. VAPOR LIQUID SEPARATOR

Figure 2

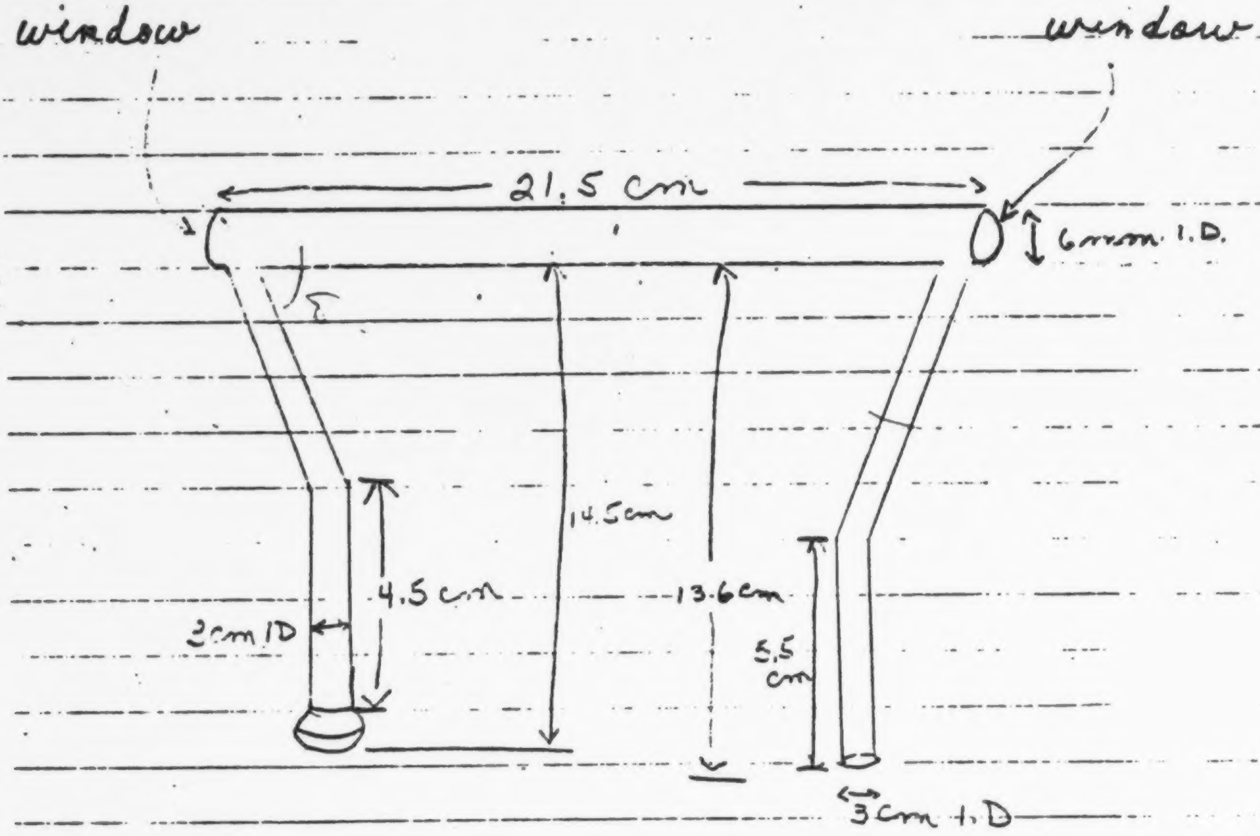
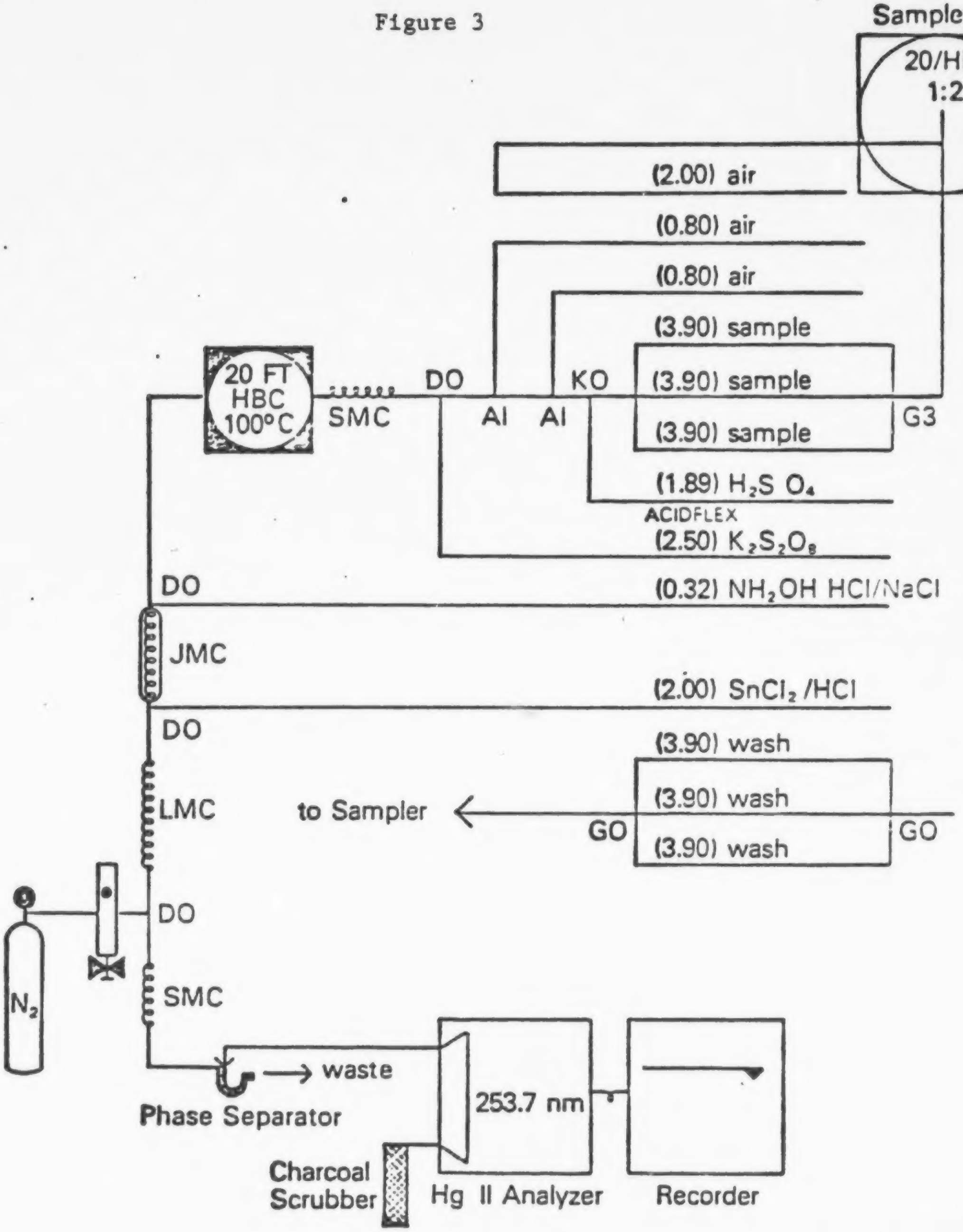

window
window
21.5 cm
6mm I.D.
14.5cm
4.5 cm
13.6cm
2cm ID
5.5 cm
3cm I.D

Figure 3


Sampler IV
20/HR
1:2
(2.00) air
(0.80) air
(0.80) air
(3.90) sample
(3.90) sample
(3.90) sample
20 FT
HBC
100°C
SMC
DO
AI
AI
KO
G3
(1.89) H₂S O₄
ACIDFLEX
(2.50) K₂S₂O₈
DO
(0.32) NH₂OH HCl/NaCl
JMC
(2.00) SnCl₂ /HCl
DO
(3.90) wash
(3.90) wash
(3.90) wash
LMC
to Sampler
GO
GO
DO
N₂
SMC
waste
Phase Separator
253.7 nm
Charcoal
Scrubber
Hg II Analyzer
Recorder

Determination of Total Metals in Sediments and Other Solids
CRL Method Nos. 571 to 598

Scope and Application

This procedure is applicable to the determination of calcium, magnesium, sodium, potassium, aluminum, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, manganese, molybedenum, mickel, silver, thallium, tin, titanium, vanadium, ytrium and zinc in sediments and other solids. It is not applicable to mercury, which is very volatile.

Summary of Method

One gram of the dried sample is digested with 8N nitric acid and 30% hydrogen peroxide, followed by heating with 25 ml of a strong nitric-hydrochloric acid solution to solubilize transition and noble metals. The sample and washings are diluted to 100 ml and a portion of the sample is analyzed for all metals by Inductively Coupled Argon Plasma Atomic Emission (ICAP) spectrometry or by atomic absorption spectrometry.

Equipment

Jarrell-Ash Plasma Atom Comp. 750 equipped with exit slits for spectral lines of the elements listed under Scope and Application. Plasma Assembly-Composed of Cross Flow Nebulizer, spray chamber, torch, coupling box and 1.3 kilowatt power supply.
or Atomic Absorption Spectrometer
Beakers
Hotplates (non-metallic)
Mettler PR 700 balance

Reagents

50% 8N HNO_3 (Redistilled)
30% H_2O_2
Conc HCl

Procedure

1. The dried sample from the total solids determination is ground with a porcelain mortar and pestle until the entire sample passes through a number ten mesh polypropylene sieve. The sieved sample is placed in a two ounce polypropylene bottle, capped and labeled.

2. One (1.00) gram of the sample is weighed into a 300 ml acid-washed tall form beaker. The beaker is placed in the hood.

3. 0.5 ml of 30% hydrogen peroxide and 20 ml of 8N (50%) re-distilled nitric acid are added to the beaker. A ribbed watch glass is placed on the beaker.

4. After heavy foaming subsides, the mixture is swirled to aid mixing, then placed on a hot plate and gently heated to dryness (at 95°C or less).

5. The beaker is removed from the hot plate, cooled and 25 ml of a mixture containing 50 ml of concentrated HCl, 200 ml of concentrated HNO_3 and 750 ml of deionized water is added.

6. The sample and acid mixture are heated for 15 minutes and cooled.

7. The contents of the beaker transferred are filtered through a quantitative grade filter paper such as Schlichter and Schnell white label paper, into a clean 100 ml volumetric flask. The empty beaker and watch glass are rinsed with deionized water and a clean (rubber usually contains zinc) rubber policeman is used to remove any deposits. The washings are transfered to the filter and allowed to filter into the volumetric falsk. The flask is diluted to the mark, capped, and shaken.

8. Approximately 50 ml of the sample is poured into one clean labeled 2 ounce (60 ml) polyethelene bottle and the other 50 ml into another clean, labelled 2 ounce polyethylene bottle. (One of the 2 ounce bottles are saved in case of re-checking at a later date).

9. The bottle contents are analyzed directly by aspiration into the ICAP (CRL Method Nos. 504 to 570 attached) or by AA. The ICAP procedures enable 21 metals to be determined simultaneously with about 10-12 ml of sample. If the same number of samples are done by AA, a much greater volume is required.

10. Some samples will require dilution from 1 to 10, 1 to 100 and even greater.

11. Results for calcium, magnesium, sodium and potassium are reported in milligrams per gram (mg/g) dry basis, whereas results for all other metals are reported as mg/kg (same as ug/g) dry weight basis.

Quality Control

A blank, duplicate and spike for every ten samples are carried through the same procedures as the samples.

The manufacturers instructions are followed for both the ICAP and AA procedures.

The balance is set to zero before and after each reading.

Calculations

Using the ICAP

$$\text{mg/kg (ug/g) dry basis} = \frac{\text{1g/100 ml} \times \text{ICAP Reading in ug/l}}{10}$$

References

1. Manual of Methods for Chemical Analysis of Water and Wastes, United States Environmental Protection Agency, Office of Technology Transfer, 1974, pp.78-155.

2. "Simultaneous Multielement Analysis of Liquid Samples by Inductively Coupled Argon Plasma Atomic-Emission Spectroscopy", United States Environmental Protection Agency, Region V, Central Regional Laboratory, Chicago, IL (unpublished).

3. "Analysis of Sediment Samples for Cadmium, Chromium, Copper, Iron, Manganese, Nickel, Lead and Zinc using Inductively Coupled Argon Plasma (ICAP) Detection", Kirkpatrick, James C., Morris, John V., United States Environmental Protection Agency, Region V, Central Regional Laboratory, Chicago, Illinois, November 1978 (unpublished).

Determination of Total Metals in Water
and Wastewaters by Plasma Spectrometry
CRL Method Nos. 504-570

Scope and Application

This procedure is applicable to the determination of calcium, magnesium, sodium, potassium, aluminum, barium, berylium, boron, cadmium, chromium, cobalt , copper, lead, manganese, molybdenum, nickel, silver, thallium, tin, titanium, vanadium, ytrium and zinc in water and industrial municipal wastewaters.

Summary of Method

The sample is digested with 8 N nitric acid to near dryness followed by additional heating with HCl to solubilize transition and noble metals. The sample is cooled, diluted to 50 ml and analyzed using Inductively Coupled Argon Plasma Atomic Emission Spectrometry (ICAP). The alkali metals concentrations are expressed in milligrams per liter, whereas concentrations for other metals are expressed in micrograms per liter. Twenty-two metals are routinely analyzed.

Equipment

Jarrell Ash Atomcomp 750. Inductively coupled argon plasma emission spectrometer consisting of:

a. RF generator

b. Plasma housing

   1. Water-cooled induction coil
   2. Quartz torch
   3. Cross-flow nebulizer
   4. Spray chamber

c. Direct reading spectrometer

   1. Entrance slit
   2. Refractor plate at entrance slit
   3. Grating
   4. Exit slits
   5. Phototubes.

d. Computer for instrument control

e. Data output device.

300 ml tall form beakers
Mettler PR 700 Balance
Corning Hot Plates

Reagents, Water, Glassware and Standards

Redistilled Nitric Acid (1:1-8 Normal).
Hydrochloric Acid (1:1), Reagent Grade.

Glassware: Beakers for digestion, after being run through diswasher, are rinsed with distilled water and placed in an aqua regia bath for at least two hours. They are then rinsed thoroughly and allowed to air dry. The chemist performing the digestion will select his or her beakers and give each a hot acid wash by following then with 1:1 HCl and placing on the hot plate for at least one half hour.

The laboratory distilled water is passed through an ultrapure mixed-bed resin column before use. All water used unless otherwise stated, has been passed through the mixed-bed resin (Super Q Water).

Standards: All standards are diluted from Fisher 1000 ppm Atomic Absorption standards with the exception of silver and beryllium (varian) and Yytrium (made from ytrium nitrate ($Y(NO3)3$).

Standards used for the ICAP Calibration Procedure

S000:	Mixed-bed resin water (super Q water)
S001:	One ppm in all elements except silver and calcium
AGCA:	1 ppm silver and 10 ppm calcium, made fresh daily.
1000:	1000 ppm calcium (Fisher)
XXXX:	1000 ppm iron (Fisher), FFFA matrix only.

Procedure

1. A designated aliquot (usually 50 ml) of well-shaken and preserved sample (pH<2) is poured off into a 300 ml tall-form beaker. Normal procedure is to place the beaker on an automatic-tare balance and deliver 50 g - drawing off excess with a disposable pipet. (This procedure assumes the sample is of sufficiently low concentration that the specific gravity is not appreciably greater than one. The purpose of a mass determination rather than a volume one is to eliminate cross-contamination). After the addition of 6 ml of 8N redistilled HNO3, to the sample a ribbed beaker cover is placed on the beaker and the sample is heated to near dryness. (The sample is not taken to complete dryness to avoid the loss of boron). If the residue is dark colored after cooling, an additional 6 ml of 8N HNO3 is added and the sample is reheated. This process is continued until no color change is detected.

2. Following the digestion, 5 ml of 1:1 HCl is added and the residue is dissolved and/or placed in suspension by warming on a hot plate. After cooling, the sample is transferred to a pre-tared 2 ounce polyethylene bottle and diluted up to 50 g. If some solids remain undissolved, the sample is filtered into a 50 ml volumetric and then transferred to a polyethylene bottle for subsequent analysis.

3. Operating Conditions

a. Incident RF power	1.1 kw
b. Reflected RF power	mimimized (<10 w)
c. Plasma observation height	15 mm above load coil
d. Horizontal observation position...	center
e. Aspiration Argon flow rate	0.6 L/min
f. Plasma Argon flow rate	22 L/min

4. ICAP Standardization Procedure and Sample Analysis.

Following startup, the instrument is profiled with the mercury monitor. The micrometer reading is recorded on the sheet with the interelement correction values for the day.

The matrix is brought onto core and time and date established. The available matrices are:
CCAS: correction for calcium
FEAS: correction for calcium and iron
KlAS: correction for calcium and iron and outputs potassium.

The Q-string QEGGGAB is set for standization. This string of commands will erase the burn buffers, execute three burns, average them, and print the average on the teletype.

(It has been found that examining the standards in background mode allows a better judgement of the noise in a given channel).

5. The standards cited above are run. Once it has been verified that the standards check, the values for interelement correction for iron and calcium are recorded and entered via the data base manager. In actual operation it is possible that these may vary only slightly (5%) from day to day, in which case they need not be entered.

Upon return to the operating system, the matrix is recalled and the blank and 1 ppm standard are checked. If these remain with in standardzation, an instrument AQC solution is measured. This AQC solution is simply the waste from the drain of the nebulizer, collected and held until it is deemed stable. The values for this solution are recorded in a log book and compared with previous values. This is a check for gross operator error during standardzation.

6. Once these criteria have been satisfied, the instrument is ready to run samples. The blank and 1 ppm standard should be checked every 30-45 min to establish that the instrument has not drifted. The blank should also be checked if values above detection limits are found for the field blanks or digested laboratory blanks.

7. Samples are aspirated for 45 seconds before executing the Q string QEGC which perform a single burn followed by output in concentration mode which includes interelement corrections. Longer flush times, may be desired for samples which follow high (>500 ppm) iron samples or high (>1000 ppm) sodium samples. No other elements have been encountered in sufficient quantities in real samples to result in noticeable memory effects.

8. Duplicates and spikes should be checked against the corresponding samples before continuing. This is to establish whether deviations occur in the digestion or measurement of samples on the ICAP. If it is found that the digestion is not at fault, restandardization on the ICAP is recommended.

9. Samples at high levels are routinely diluted 10-fold to determine if results for all elements are valid or the result of intererence not accounted for by the matrix IECC's.

   The paper tape from the teletype is read into the DG NOVA and the report plus QC check is performed by programs written in BASIC.

Quality Control

Four types of quality control samples are put through the digestion process at the same time as the samples. In a typical run of forty samples there are in addition, four blanks, 4 AQC solutions, 2 duplicates, 2 spikes.

1. Blanks: These are simply the laboratory super Q water carried through the same digestion process as the samples. The blank data is summarized periodically and is used to determine detection limits for the method (average and 2 standard deviations).

2. AQC Solutions: A series of solutions were made to cover the ranges measured for each parameter. These were arranged in Youden pairs approximately as follows: 10 ppm - 8 ppm; 1 ppm - 800 ppb; 100 ppb - 80 ppb. Two pairs of these solutions are digested as part of the run. This is separate from the instrument AQC and calibration procedure mentioned earlier.

3. Duplicates: Two samples are chosen to be analyzed as duplicates are carried through the digestion process. The results for these are expected to be within 10% of each other for each element, for concentrations in the working range (blank one + 10 standard deviations).

4. Spikes: Two samples are chosen to be analyzed as spikes. A table of spike concentrations in terms of final concentrations is formulated Spike recoveries are determined if the sample is less than 200% of the added spike.

Routine Maintainance

Following four days of operation the torch and nebulization spray chamber should be acid washed. Before the torch is removed and after it is replaced, statistical programs are run to determine the standard deviation of all the lines when aspirating blank water. Dark currents are also examined in this manner. A reading of the profile meter is taken for each element both before and after cleaning while aspirating both blank water and the 1 ppm standard. When the torch is replaced, coarse alignment is made using a 1000 ppm yttrium standard to center the image on the slit. Fine adjustment of the mirror is made by maximizing the signal to noise ratio on the lead line.

Once a month, statistical programs are run to maintain an historical record of intensities obtained on each line for the series of standards.

Calculations

These are done by the computer program (written in basic) including insertion of dilution factors to give results in mg/l for calcium, magnesium and sodium and ug/l for the other metals.

Reference

1. Manual of "Methods for Chemical Analysis of Water and Wastes", U.S. Environmental Protection Agency, Office of Technology Transfer, 1974, Washington, DC, pp 78-155.

2. "Simultaneous Multielement Analysis of Liquid Samples by Inductively Coupled Argon Plasma Atomic - Emission spectroscopy", U.S. Environmental Protection Agency. Region V, Central Regional Laboratory, Chicago, Illinois, (unpublished).

Determination of Total Antimony, Arsenic and Selenium and Thallium in Sediments and Other Solids by Flameless Atomic Absorption
CRL Method Nos. 601, 604, 607, and 595

Scope and Application

This method is applicable to the determination of total antimony, arsenic and selenium and thallium in sediments and other solids.

Summary of Method

One gram of the dried sample is digested with 8N nitric acid and 30% hydrogen peroxide, followed by heating with 25 ml of a strong nitric-hydrochloric acid solution to solubilize transition and noble metals. The sample and washings are diluted to 100 ml and analyzed by atomic absorption, using the graphite furnace flameless standard additions technique.

Equipment

Atomic absorption spectrometer with graphite furnace attachment and autosampler hotplates (non-metallic)

Beakers

Mettler PR 700 balance

Eppendorf pipets

Reagents

50% 8N HNO_3 (redistilled)

30% H_2O_2

Conc HCl

Procedure

1. The dried sample from the total solids determination is ground with a porcelain mortar and pestle until the entire sample passes through a number ten mesh polypropylene sieve. The sieved sample is placed in a two ounce polypropylene bottle, capped and labeled.

2. One (1.00) gram of the sample is weighed into a 300 ml acid-washed tall form beaker. The beaker is placed in the hood.

3. 0.5 ml of 30% hydrogen peroxide and 20 ml of 8N (50%) redistilled nitric acid are added to the beaker. A ribbed watch glass is placed on the beaker.

4. After heavy foaming subsides, the mixture is swirled to aid mixing, then placed on a hot plate and gently heated to dryness (at 95° or less).

5. The beaker is removed from the hot plate, cooled and 25 ml of a mixture containing 50 ml of concentrated HCl, 200 ml of concentrated HNO_3 and 750 ml of deionized water is added.

6. The sample and acid mixture are heated for 15 minutes and cooled.

7. The contents of the beaker transferred are filtered through a quantitative grade filter paper such as Schlichter and Schnell white label paper, into a clean 100 ml volumetric flask. The empty beaker and watch glass are rinsed with deionized water and a clean (rubber usually contains zinc) rubber policeman is used to remove any deposits. The washings are transfered to the filter and allowed to filter into the volumetric flask. The flask is diluted to the mark, capped and shaken.

8. Approximately 50 ml of the sample is poured into one clean, labeled 2 ounce (60 ml) polyethylene bottle and the other 50 ml into another clean, labeled 2 ounce polyethylene bottle. (One of the 2 ounce bottles are saved in case of re-checking at a later date).

9. A portion of the sample is removed and diluted 1 to 10 prior to analysis. (This is to lessen the chloride matrix effects in the sample).

10. The sample is analyzed by flameless atomic absorption using the Standard Additions Technique (CRL Methods 594, 600, 603 and 606, Attached)

11. Generally, 20 microliters of the sample is injected into the furnace followed by three spikes of sample plus the element of interest.

Quality Control

A field reagent blank and duplicate is analyzed with each group of ten samples. The standard additions technique involves spiking the real samples to compensate for matrix effects, therefore, spike and recovery values are received for every sample. The manufacturers instructions are followed for the instrument. The balance is set to zero before and after each reading.

Calculations

$$\text{mg/kg (ug/g) dry basis of metal} = \frac{\text{1 g/100 ml x least squares value x dilution factor}}{10}$$

REFERENCES

1. Manual of Methods for Chemical Analysis of Water and Wastes, United States Environmental Protection Agency, Office of Technology Transfer, 1974, pp. 78-155.

2. "The Determination of Antimony, Arsenic, Beryllium, Cadmium, Selenium, Lead, Silver and Tellurium in Environmental Water Samples by Flameless Atomic Absorption", Metals Section, United States Environmental Protection Agency, Region V, Central Regional Laboratory, Chicago, Illinois.

3. "Determining Selenium in Wastes, Wastewaters, Sediment and Sludge by Flameless Atomic Absorption Spectroscopy", Martin, Theodore D., Kopp, John F., Atomic Absorption Newsletter, Volume 14, No. 5, September-October 1975.

4. "Quality Control Summary for Graphite Furnace Analysis", Meszaros, Timothy, United States Environmental Protection Agency, Region V, Central Regional Laboratory, Chicago, Illinois, June 1977, unpublished.

Determination of Total Antimony, Arsenic, Selenium and Thallium in Water and Wastewater by Flameless Atomic Absorption

CRL Method Number 600, 603, 606, and 594

Scope and Application

This method is applicable to the determination of total antimony, arsenic, selenium, and thallium in surface and drinking water, wastewaters and industrial wastes.

Summary of Method

Regular samples are analyzed by Flameless Atomic Absorption followed by equal volumes of the regular samples spiked with a blank and standards containing the element of interest to correct results for possible unknown interferences. Sample values range generally from 2 to 20 ug/l for the elements (higher ranges upon dilution of the samples). Recoveries range from 90 to 110% at a concentration level of 10 ug/l.

Equipment

Perkin Elmer Model 503 Atomic Absorption Spectrometer equipped with an HGA 2100 Graphite Furnace, deuterium background corrector, Strip Chart Recorder Model PE 056 and AS1 Automatic Sampler.

Electrodeless Discharge Lamp (EDL) for Antimony, Arsenic and Selenium

Hollow Cathode Lamp for Thallium

Eppendorf Pipettes (or equiralent)

Disposable 1 ounce plastic cups

Cups to fit AS1 Sampler

Data General NOVA, 840 Minicomputer

Reagents, Standards, Distilled Water and Glassware

Distilled Water: The laboratory distilled water is passed through an ultrapure mixed-bed resin column before use. All water used unless otherwise stated, has been passed through the mixed-bed (super Q) water resin.

Glassware: Beakers and glassware for standards run through dishwasher, are rinsed with distilled water and placed in an aqua regia bath for at least two hours. They are than rinsed thoroughly and allowed to air dry. The chemist performing the test will select his or her beakers and glassware and give each a hot acid wash by filling them with 1:1 HCl and placing on the hot plate for at least one half hour.

Redistilled Nitric Acid (1:1), 8 Normal

Hydrochloric Acid, Reagent Grade

Calibration Standards
Four standards per element are prepared fresh daily from a stock solution of 1 ppm of the element of interest.

Stock solution: Dilute to 100 ml in a clean volumetric flask 100 ul of 1000 ppm Fisher standard or equivalent with deionized water from the prep lab column or equivalent plus 1 ml of 1:1 redistilled HNO_3. For Arsenic and Selenium also add 1 ml of 1000 ppm Nickel Standard.

Calibration Standards: Calibration standards consist of a reagent blank [a 1% solution of 1:1 redistilled HNO_3 (+ 1 ml 1000 ppm Ni standard if As, Se)] and three standard solutions for the method of additions spiking. These usually range from 5 to 80 ppb and are listed for each element under it's conditions for analysis listed later in this paper. All are appropriate dilutions of the 1 ppm stock solution in 1% 1:1 redistilled $HN0_3$ brought to a final volume of 100 ml, 1 ml of 1000 ppm Ni standard is added if As, Se, are to be analyzed. e.g.: 1000 ul (1 ml) of stock solution (1 ppm) in 100 ml = 10 ppb.

Note: Eppendorf disposable pipettes are used for all additions. Thorough shaking to mix the solution is required. Acid is always added to the volumetrics containing some deionized water first before the nickel or stock solutions.

Control Standards: For arsenic and selenium analysis a lab control standard is analysed.

The LCS is spiked with only reagent blank plus the two highest calibration standards on a 500 ul 1:1 basis.

The spectro might appear as: A least squares fit of the peak height versus spike concentration would produce a negative concentration value, (see section on calculation of data). In actuality, negative concentration values are what one wants, the absolute value is reported.

Lab control standards (LCS) have "known" values

Arsenic: 26 ug/l
Selenium: 26 ug/l

Note: Historical data on the selenium LCS has averaged 19-20 ug/l after more than a year of analysis. LCS results are also kept and tabulated, as statistical analysis on the results will be used later in quality control.

Instrument Operational and Standardization Instructional Procedures

1. Turn on the PE 056 strip chart power to amp.
   Reserve setting to serve until ready to record peaks.

2. Turn on the HGA 2100 Power.

3. Turn on the 503 AA Power.

4. Turn on the Supply.
   By turning valve from overhead gas columns clockwise, check to make sure gas is on by opening valve on HGA Power Supply and observing flowrate setting of 40. Once argon is on, close valve on HGA Power Supply to save on argon use. Check argon supply before daily run by noting supply in the mechanical room.

5. Turn on water.

6. Turn on Hollow Cathode or Electrodeless Discharge Lamp (see Table 1 for Instrumental Settings).

   HCL - Set current to lamp at rated amperage
   EDL - Set power setting to approximately 1.5 watts below recommended power setting on lamp.

   Note: Once power supply is turned on lamp is not necessarily on.

   Lighted match or other source of light if placed in front of lamp will usually initiate EDL lighting.

   If power control on supply is slowly turned clockwise, meter may show increase in power to lamp then suddenly increase, signifying lamp has lit or meter may even decrease at five below the zero point and then suddenly increase.

   By setting lamp 1.5 watts below recommended power setting, will allow lamp warm-up drift (.5 watts) until steady power output is attained (by noting deviation of meter on 503 AA in Reverse Mode).

   Althrough still 1 watt below recommended setting, this is at first acceptable, since at the higher recommended setting the Deuterium Arc Lamp cannot always balance the energy of the EDL.

   Options - Element of Choice

7. While waiting for the HCL or EDL to warm up 15 minutes and approximately 1.5 hours several instrumental parameters may be set.

8. Slit width

9. HGA 2100 Program

   Time for the three segments of cycle
   Temperatures
   Atomisation time temperature and charring (ashing)
   Furnace parameters used in this laboratory are given in Table I.

Drying time, temperature and notably charring time are a function of sample type. A sample with high particulate matter, especially of an organic nature may be better analyzed if charred for a longer time. Smoke and thus light scatter will be minimized. The limiting factor is loss of the element of interest by removing the matrix in which the metal is contained. The list at end of paper lists time and temperature which provide adequate sensitivity for routine analysis.

10. Aliquot volume: The AS-1 at present has two pump sizes - 20 ul and 50 ul The choice of these is based upon the sensitivity required.

11. Strip chart range: Once the lamp (HCL or EDL) is sufficiently stable (EDL's drift notoriously during warm-up) the following parameters can be set.

Wavelength: With 503 AA in Reverse Mode (observing energy of lamp on AA Energy meter) adjust wavelength to maximize energy reading.

One may not notice any fluctuation on meter if the meter is on the low end. Increasing gain until a midscale reading is attained will allow observation of meter deflection (in Reverse Mode!).

Lamp Position: Again, we want to maximize the lamp energy reaching the detector. Remain in Reverse Mode and adjust vertical and horizontal lamp positions until maximum meter reading is achieved.

Energy Maximization:

A. Set meter needle to fixed reference point on the scale using the gain control knob while remaining Reverse Mode, (preferably in the green area of the scale).

B. Release Reverse Mode and adjust Deuterium Arc Lamp energy (now being observed on the meter, using the push buttons on the D_2 lamp power supply) to the reference point on the scale to which the HCL or EDL energy had previously been set. This is balancing the sample and background beams energies.

   More often than not, the D_2 lamp energy cannot be balanced at the same level as the EDL or HCL if the EDL, HCL is set at it is recommended value. This can be rectified in two ways.

   a. Decreasing EDL power or HCL current. Note: earlier it was recommended that the EDL's be set at 1.5 watts below nominal power setting. After 0.5 watt drift upward, the lamp can usually be left at this setting and still balance the beam energies.

   b. Sometimes if a high EDL or HCL energy level is desired for which the D_2 lamp energy cannot be balanced, the line source energy may be set at a reference point within the energy may be set at a reference point within the energy meter's given area and the D_2 lamp energy set as high as possible. This is usually necessary when operating with an older lamp which requires higher energy output to offset baseline noise.

Note: Be careful not to allow the dark portion of the neutral density filter into the optical path. This can be checked blocking off the light from the line source and observing the light from the D_2 lamp with the mirror held at the end of the furnace.

C. Points A and B have to be repeated at regular intervals due to drift. Once the line source reference point is reset and the best effort made with the D_2 lamp, press the Auto Zero to reset the baseline.

There are a few days when the beam energies cannot be balanced; This should not deter one from analyses. Good results can most readily be obtained despite minimal D_2 lamp capabilities.

13. Mechanics of Analysis

At this point calibration standards have been made, line source (EDL or HCL) has been warmed-up, the energy of the sample and background beams have been equalized (or best possible) and the baseline is not drifting severely, or is extremely noisy (may check by having recorder on servo and switching from Auto to Manual or HGA Power module). Depending on the type of lamp, to attain all this may take from 30 minutes (HCL operation) to 1.5 hours (good EDL operation).

A. Sampler alignment (may be done any time before analysis)

1. With AS-1 Box Power off manually lift sampler arm, bring to position as if to draw sample and take towards furnace.

2. With supplied mirror placed at right end of furnace observe if sampler arm easily is placed into furnace without hitting sides or bottom of graphite tube.

3. If out of alignment, release lock under auto sampler and adjust position with knobs at end of sampler table.

Also if necessary, adjust depth of sampler arm, see manual on auto sampler position adjustment for placement of controls.

B. Graphite tubes

1. Graphite tubes are always conditioned before analysis begins.

a. Make sure water and argon is turned on.

b. Condition by performing a high temperature "burn" for approximately 10 seconds.

2. It never hurts to give older tubes a high temperature "burn" for a few seconds before analysis either, as the graphite may be contaminated from the previous day's analyses.

Note: New tubes should be used whenever lead is analyzed, due to lead contamination.

C. Furnace blank

1. Be sure recorder is on Servo.
2. Manually press Program button on HGA Power Supply to initiate a burn cycle with its specified temperatures and times.
3. If the spectro shows a deflection above baseline (a peak) run another high temperature burn and repeat furnace blank.

14. Mirrors and Glass

Once a month

1. Photometer windows
2. Furnace end windows
   (may require periodic cleaning as sample with smoke tend to leave particulates).

Less Frequently

1. Mirrors - clean with ethanol plus lens tissue, careful not to move.

Furnace

1. Graphite tube - change often as needed. Note severe cracking at spots other than the injection port. Also note the function of sample volumes used, times and temperatures and frequency of high temperature burns.
2. Graphite contact rings - rarely need replacement. Good for six months or better. If lead is continously analyzed, change more often.

D_2 Arc Lamp

If severely bad performance of the D_2 arc lamp is encountered, a service call is usually necessary. The lamp, the small mirror directly above the lamp housing, and the adjustable slit (not to be confused with the slit in the monochrometer housing) may need alignment.

Procedure

Reagent blank plus three calibration standards

1. All samples are run using the method of standard additions, whereby a sample is spiked with varying concentrations of the element of interest.

2. Using the 1 oz. plastic cups, for the three calibration standards, place 50 ul of each standard with an Eppendorf pipette into three cups being careful not to lose any standard from "splashing".

3. Place 500 ul of reagent blank into each cup so that there is a 1:1 spike performed for each standard.

4. Mix well.

5. Begin injections with the reagent blank alone, then the three spiked standards.

   Assuming the Auto Sampler is being used, place 1 ml of the four solutions into four 2 ml cups in increasing order of spike concentration. Place the cups on an empty sample wheel and press the start/stop button on the AS-1 box. It is assumed that the AS-1 box has been powered by pressing the red Power button and noticing the flashing light in the start/stop button has gone out. The flashing takes place while the digital electronics are being set.

6. The resultant run should appear as shown in Figure 1.

   Note the linearity of the peak heights. If "perfectly" linear, with no reagent blank deflection from baseline, the calculation from plotting peak height versus spike would produce an intercept of zero indicating zero concentration for the element of interest in the reagent blank. Unfortunately, due to variation in peak heights from actual contamination of glassware, graphite tubes, etc. and/or detector response fluctuation, we often get a reading of either positive or negative concentration. The calculated result of "reagent blank concentration" are to be kept for calculation of detection limits (X + o).

   where: X - the mean calculated concentration
   o - the standard deviation from the mean

7. All samples are analysed as the LCS were - method of additions with reagent blank plus the two highest calibration standards.

8. Prepare ten samples at a time.

9. Inject 500 ul of reagent blank into the first cup beside each sample.

10. Next inject 500 ul of the next calibration standard into the second cup next to a sample.

Figure 1

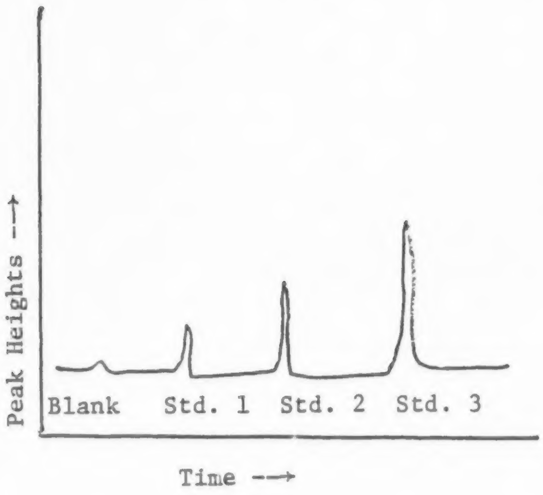


Illustration of Peak Heights

11. Inject 500 ul of the last calibration standards into the third cup next to each sample.

    These procedures save Eppendorf tips and your time.

12. Shake each sample in turn and inject 500 ul of sample into each of the three cups next to it.

13. After 10 samples are prepared this way, mix each cup's contents by shaking or in the case of viscous samples, stir with the Eppendorf pipette with a clean tip.

14. Fill a sample wheel with the 10 samples (30 cups), place on the turntable, check again for energy beams being balanced and any other conditions, press start/stop on AS-1 box to begin analysis.

Quality Control

A field reagent blank and duplicate of one of the ten samples are analyzed. Data is only good when it passes quality control measures to assure accuracy.

1. Acceptable data are obtained when peak heights are linear within statistical limits for calibration on stds. as well as real samples.

2. When Lab Control Standards (LCS) - are run with each group of twenty samples and are within acceptable limits of variation.

3. Duplicates - agreement should be within limits set in Quality Control Manual (generally within 10%).

Quality Control and Instrument Logbook

In order to properly keep track of samples analyzed, acquire data for statistical calculation of quality control parameters and keep record of maintenance of the AA, a QC and Logbook is kept. The book consists of various sections.

Section 1. is completed at the end of each day.

Section 2. is also entered into each day. The frequency at which the analyst cares to use the running accumulation of data is left to his or her discretion.

Section 3. is entered only when notable changes in daily opeation service calls or operator maintenance occurs.

Calculations

Each peak height is measured in millimeters. Provided a sample's peak are proportionally linear a least squares fit program to calculate the concentration may be used.

Graphically, peak heights are plotted as a function of spike concentration (actually spike plus sample concentration). The negative concentration axis intercept being the concentration of the sample. The best fit line of the calibration standards normally intercepts at the (0,0) point. It is the added absorbance of the sample which changes the negative concentration axis intercept.

A linear least square fit program accomplishes the same calculation and the present program on the NOVA is:

ID: AAA1
Name: "Flameless"

Results must at present be transcribed from the CRT screen to paper as no hard copy report is now written.

A data storage file is not included either so that the raw spectra must be saved to record data at a later date.

References

1. "The Determination of Antimony, Arsenic, Berylium, Cadmium, Selenium, Lead, Silver and Tellurium in Environmental Water Samples by Flameless Atomic Absorption", Metals Section, United States Environmental Protection Agency, Region V, Central Regional Laboratory, Chicago, Illinois, (unpublished).

Table I
Instrumental Settings For the Determination
of Arsenic, Antimony, Selenium and Thallium

	As	Sb	Se	Tl
Wavelength, NM	193.7	217.6	196.0	276.8
Bandpath, nm	0.7	0.2	0.7	0.7
EDL Power, W	8	8	6	
Hollow Cathode Lamp, Current				20 milliamps
Drying Temp. °C (Time, sec.)	125(60)	125(60)	125(60)	175(40)
Charring Temp., °C (Time, sec.)	1000(40)	1000(40)	1000(40)	400(40)
Atomize Temp., °C (Time, sec.)	2700(5)	2200(5)	2700(3)	2100(8)
Argon Gas Flow, ml/min	50	50	50	40 (interrupt)

Determination of Phenols in Sediments and Other Solids
CRL Method 417

Scope and Application

This method is applicable to the determination of phenolic compounds (except paracresols and similar parasubstituted phenols) in sediments and other solids.

Summary of Method

Phenolic compounds are manually distilled to remove interferences. The distillate reacts with buffered ferricyanide and 4 aminoantipyrine spectrophotometrically at 505 nm. An automated system is used for the color development and measurement.

Equipment

Distillation apparatus, consisting of a 500 Pyrex flat-bottom distilling flask and a Graham condenser.

250 ml or 500 ml Erlenmeyer flasks calibrated at 200 ml.

Technicon Autoanalyzer II System (See CRL Method 408, Attached)

Analytical Balance

Heating Mantles or Burners

Reagents

$CuSO_4/H_3PO_4$ Solution, 5%

10% H_2SO_4

Other Reagents - See CRL Method 408 (Attached)

Procedure

1. Steam out the distillation flasks before each use by boiling distilled water in the flasks without water running through the condenser.

2. Weigh accurately 1 to 2 grams of wet, well-mixed sediment.

3. Transfer to the distillation flask.

4. Add 100 ml of distilled water and 2 ml of 5% $CuSO_4/H_3PO_4$ solution.

5. Distill 100 ml of sample (20-35 ml of distilled water may be added to assure distillation of 100 ml of sample into the erlenmyer flask).

6. Add 1 ml of 10% H_2SO_4 and proceed with analysis using CRL Method No. 408. (Samples may be stored at 4°C for a maximum of three weeks if necessary).

Quality Control

A field blank which contains $CuSO_4/H_3PO_4$, one or more standards and a duplicate of one of the samples, are analyzed with each group of samples. If twenty or more samples are analyzed, a minimum of two field blanks, standards and duplicates are analyzed.

The analytical balance is set to zero before each sample is weighed.

The manufacturers instructions are followed for operation of the Technicon Autoanalyzer.

Calculation

$$\text{mg/kg Phenol (dry basis)} = \frac{\text{reading in ug/l} \times 1000 \text{ from Method 408} \times 100}{(\text{orig. wt. in grams}) \times \text{decimal fraction of \% solids}}$$

References

1. "Manual of Methods for Chemical Analysis of Water and Wastes", United States Environmental Protection Agency, Office of Technology Transfer, 1974, Washington, DC, p. 241-242.

Determination of Phenol in
Water and Wastewater
(Automated 4-AAP Method With Manual Distillation)
CRL Method No. 408

Scope and Application

This method is applicable to drinking, surface, saline, domestic and industrial waste waters.

Summary of Method

Phenolic compounds are manually distilled to remove interfering substances. The distillate reacts with buffered ferricyanide and 4-aminoantipyrine to form a red complex which is measured spectrophotometrically at 505 nm. An automated system is used for the color development and spectrophotometric measurements.

Interferences

Interferences from sulfur compounds are eliminated at the time of collection by acidifying the samples to a pH of less than 4 with H_3PO_4 and adding $Cu\ SO_4$.

If residual chlorine is present it is removed by the addition of an excess of $NaAsO_2$ to reduce the chlorine prior to distillation.

All other interferences are eliminated or minimized by the distillation procedure.

Sample Handling and Preservation

New polyethylene bottles are used for sample collection. (Caps must not contain phenolic resin).

Samples are preserved with 20 ml of a solution containing 50 g $CuSO_4 \cdot 5H_2O$ and 50 ml H_3PO_4 per liter of sample.

Samples are stored at 4°C.

Apparatus

Distillation apparatus, consisting of a 500 ml Pyrex flat-bottom distilling flask and a Graham condenser.

250 or 500 ml erlenmeyer flasks calibrated at 200 ml.

Technicon Auto Analyzer II (3)

Sampler IV

Pump III

Phenol Cartridge

Colorimeter containing 50 mm flowcells and 505 nm filters.

Recorder

Digital Printer.

Reagents

$CuSO_4$ preservative: Dissolve 50 g of $CuSO_4 \cdot 5H_2O$ and 50 ml of H_3PO_4 in distilled water and dilute to 1 liter. (Use 20 ml/l sample).

H_2SO_4 preservative: Add 100 ml conc H_2SO_4 to 800 ml of distilled water and dilute to 1 liter. (Use 10 ml/l sample).

Stock phenol solution: Dissolve 1.00 g of reagent grade phenol in distilled water. Add 10 ml of H_2SO_4 preservative and dilute to 1 liter. (1 ml = 1000 ug). Store at 4°C.

Intermediate phenol solution: Dilute 10 ml of stock phenol solution to 100 ml with distilled water (1 ml = 100 ug). Prepare fresh daily.

Working phenol standards: Dilute 0, 0.50, 1.00, and 2.00 ml of intermediate phenol solution to 1 liter with distilled water for blank, 50, 100 and 200 ug/l phenol standards.

NOTE: These standards should be preserved with $CuSO_4$ preservative solution if they are to be distilled. They should be preserved with H_2SO_4 preservative solution if they are to be used for instrument calibration.

Ammonia buffer: Dissolve 50 g of NH_4Cl in about 900 ml distilled water. Adjust the pH to 10.1 using NH_4OH. Dilute to 1 liter.

In NaOH: Dissolve 40 g of NaOH in distilled water and dilute to 1 liter.

Potassium ferricyanide solution: Add to 800 ml of distilled water, 2.0 g of $K_3Fe(CN)_6$, 3.75 g of KCl and 44 ml of 1N NaOH. Dissolve and dilute to 1 liter. Adjust the pH to 10.1 and add 0.5 ml of Brij-35. Store at 4°C. Filter before each use.

4-aminoantipyrine: Dissolve 0.65 g of 4-aminoatipyrine in distilled water and dilute to 1 liter. Store at 4°C. Filter before each use.

Sampler wash solution: Dilute 10 ml of H_2SO_4 preservative to 1 liter using distilled water.

Procedure

Distillation

Steam out the distillation flasks before each use by boiling distilled water in the flasks with the condenser water off.

Using a graduate, measure 200 ml of sample into each distilling flask. Also measure out one blank, one standard, and one duplicate for each run. Add 35 ml of distilled water to each flask.

Distill 200 ml of sample into calibrated erlenmeyer flasks or bottles. Add 2 ml of $H_2 SO_4$ preservative. The samples may be stored at 4°C for future analysis for a minimum of three weeks or longer.

Spectrophotometric Analysis

Set up the Technicon AA-II system as indicated in the diagram.

Calibrate the system using standards containing 200, 100, 50 and 0 ug phenol/l.

Also analyze control standards CS1 and CS2 (See paragraph 2 under Quality Control).

Analyze the distilled samples, blanks and duplicates.

Detection Limit

The detection limit is 5 ug phenol/l.

Quality Control

One standard, one blank, and one duplicate are distilled with each sample set.

After calibration of the analytical system, 2 control standards are run. They must be within control limits if the data is used. Results are recorded in the AQC book.

The date of preparation of reagents and standards is recorded in the AQC book.

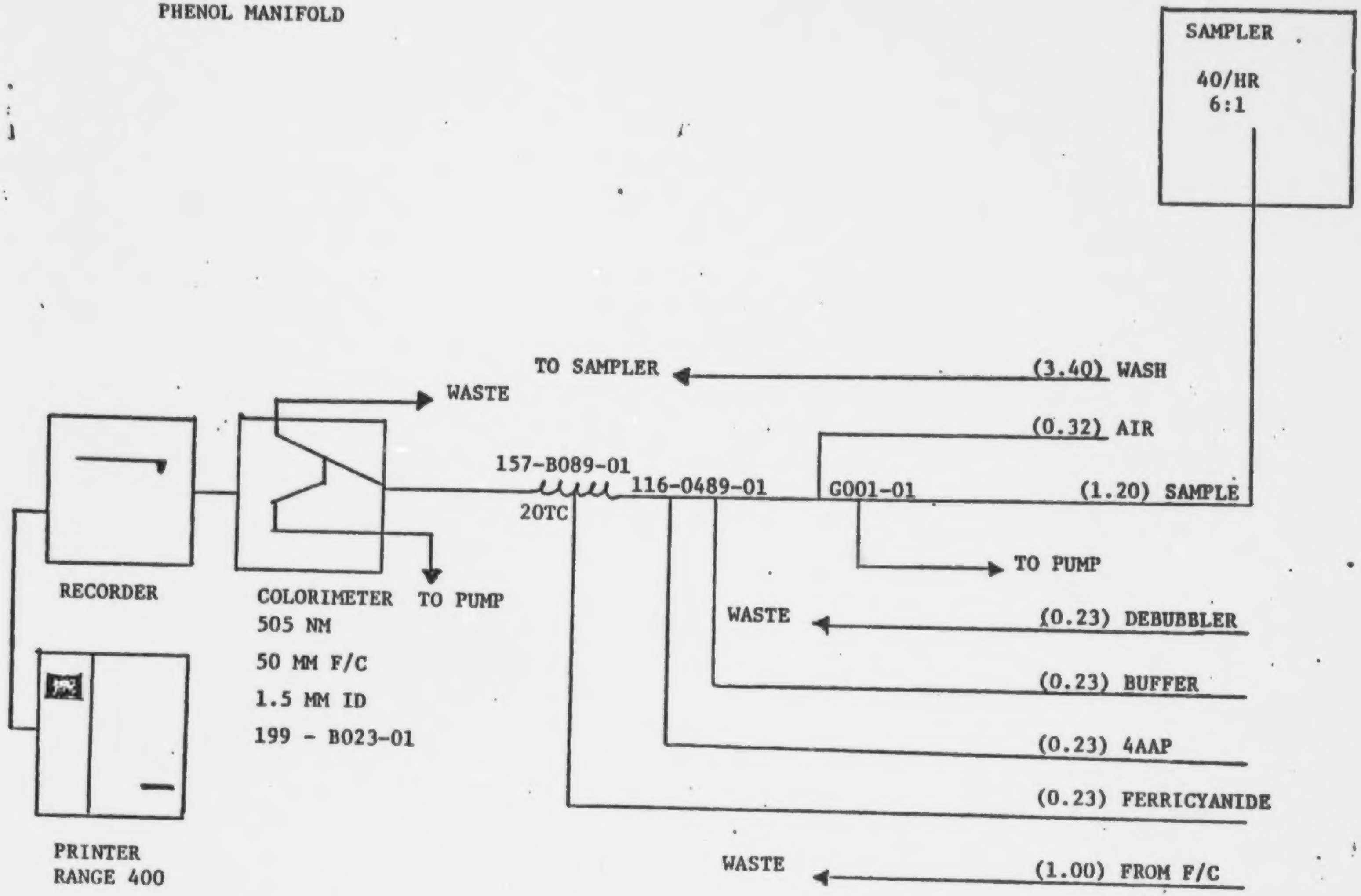
Calculations

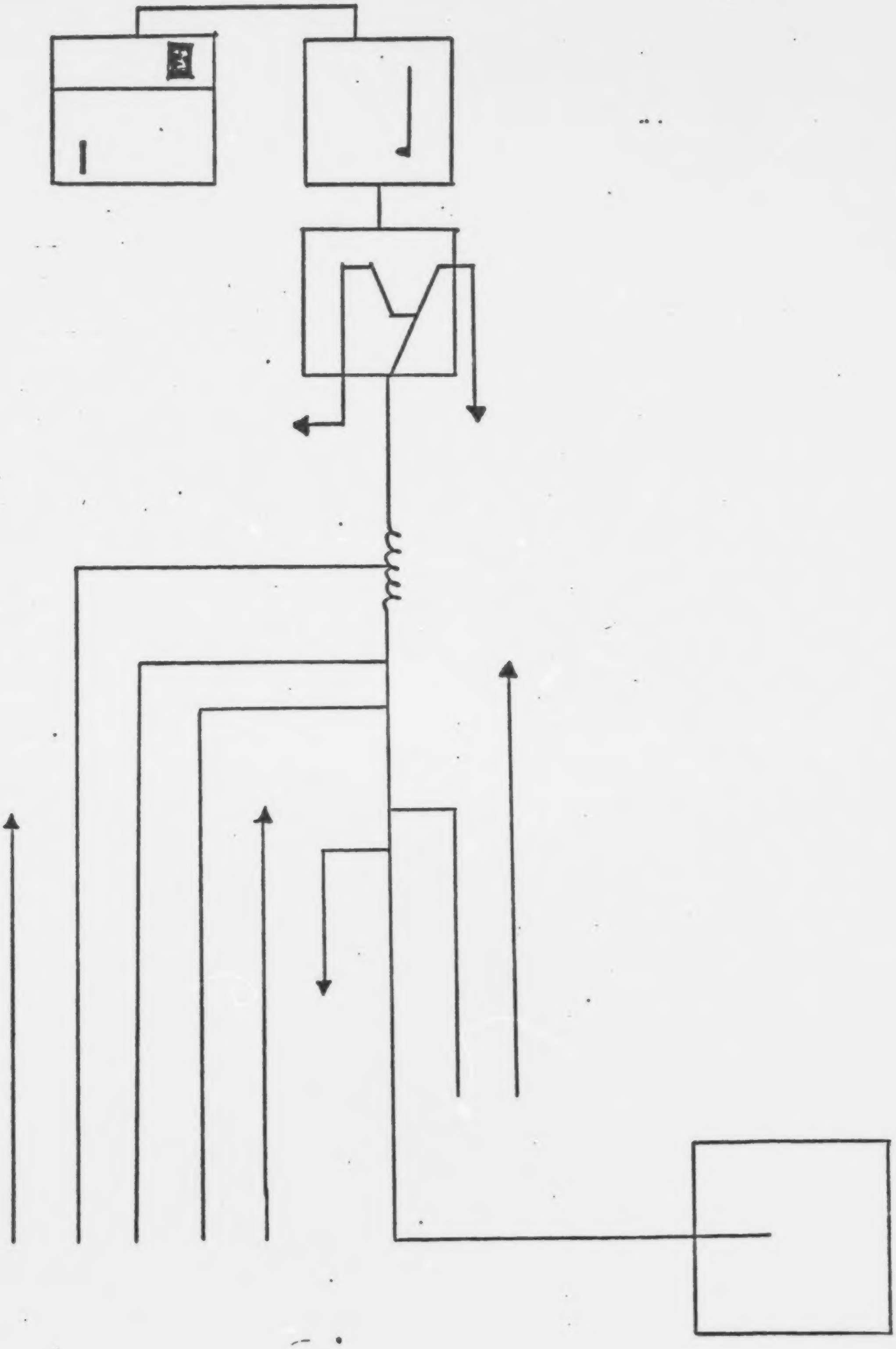
The concentration of phenol in ug/l is obtained directly from the digital printer.

References

1. "Standard Methods for the Examination of Water and Wastewater", 14th ed., American Public Health Association, New York, N.Y., 1975, p. 574.
2. "Manual of Methods for Chemical Analysis of Water and Wastes", U.S. Environmental Protection Agency, Cincinnati, OH, 1974, p. 241.
3. Industrial Method No. 127-71W, Technicon Industrial Systems, Tarrytown, N.Y., 1972.
4. Carter, M.J. and Huston, M.T., "Preservation of Phenolic Compounds in Wastewaters" (unpublished), U.S. Environmental Protection Agency, CRL, Chicago, IL, 1977.

PHENOL MANIFOLD


SAMPLER
40/HR
6:1
TO SAMPLER
(3.40) WASH
WASTE
(0.32) AIR
157-B089-01
20TC
116-0489-01
G001-01
(1.20) SAMPLE
TO PUMP
RECORDER
COLORIMETER
505 NM
50 MM F/C
1.5 MM ID
199 - B023-01
TO PUMP
WASTE
(0.23) DEBUBBLER
(0.23) BUFFER
(0.23) 4AAP
(0.23) FERRICYANIDE
WASTE
(1.00) FROM F/C
PRINTER
RANGE 400



Determination of Phenols in Water
Automated Distillation and Automated Colorimetry
CRL Method 414

Scope and Application

This method is applicable to the determination of phenolic compounds (except paracresols and similar parasubstituted phenols) in lake, surface, waters, elutriates and other water mediums which are not governed by the National Pollution Discharge Elimination System.

Summary of Method

Phenolic compounds are distilled on the autoananlyzer at 150°C to remove interferences. The distillate reacts with buffered ferricyanide and 4-aminoantipyrine spectrophotometrically at 505 nm. An automated system is used for color development and measurement. This method involves the determination of phenols in the ranges of 30-200 ug/l using a completely automated system.

Equipment

Techicon Auto Analyzer II

- Sampler IV
- Pump II
- Phenol Cartridge
- Heating Bath With Distillation Coil
- Colorimeter With 50 mm Flow Cells and 505 nm Filters
- Recorder
- Digital Printer

Reagents

Distillation Reagent (Techicon No. T01-5017)

Phosphoric Acid, 85% (H_3PO_4)	100 ml
Distilled Water, q.s.	1000 ml

Preparation: Carefully add 100 ml of phosphoric acid to 700 ml of distilled water. Dilute to one liter with distilled water.

Buffered Modified Potassium Ferricyanide	2.0	
Potassium Ferricyanide ($K_3Fe(CN)_6$)	1.0	g
Boric Acid (H_3BO_3)	3.1	g
Potassium Chloride (KCl)	3.75	g
Sodium Hydroxide, 1N (NaOH)	44	ml
Distilled Water, q.s.	1000	ml
Brij-35* (Technicon No. T21-0110)	0.5	ml

Preparation: Add to 800 ml of distilled water, 2.0 g of potassium ferricyanide, 3.1 g of boric acid, 3.75 g of potassium chloride and 44 ml of 1N sodium hydroxide, Dissolve and dilute to one liter with distilled water. Adjust the pH to 10.1 and add 0.5 ml of Brij-35.

4-Aminoantipyrine (Technicon No. T11-0021)

4-Aminoantipyrine ($CH_3NN(C_6H_5)COC(NH_2):CCH_3$)	0.65	g
Distilled Water, q.s.	1000	ml

Preparation: Dissolve 0.65 of 4-aminoantipyrine in 800 ml of distilled water. Distilled water.

Standards

Stock Standard A, 100 mg/l

Phenol (C_6H_5OH)	0.100	g
Hydrochloric Acid, 0.05N, q.s	1000	ml

Preparation: Transfer into a one liter volumetric flask 0.100 g of phenol. Use 0.05N hydrochloric acid to assist in the transfer and mix until dissolved. Dilute to volume with 0.05N hydrochloric acid.

Stock Standard B, 10 mg/l

Dilute 100 ml of Stock A to one liter with distilled water.

Working Standards

ml Stock B	ug/l
1	100
2	200
3	50

Preparation: Pipette stock B into a 100 ml volumetric flask and dilute to volume with distilled water.

Note: The stock standard B and the working standards are not stable and should be prepared fresh twice daily.

Procedure

1. Following sample arrival, unpreserved samples should be preserved with 1 ml per liter concentrated sulfuric acid (H_2SO_4) if analysis is not to begin immediately.

2. Fill the Technicon Sampler IV cups with sample (usually 8 to 10 ml), blank and working standards ranging from 30 to 200 ug/l.

3. Use a wash cycle containing 1 ml H_2SO_4 per liter.

4. Set the temperature of the heating bath to 150°C.

5. Adjust the flow of cooling water through the distillation apparatus to approximately 750 ml per minute at 14°C (See Technicon Publication Number TA 1-0213-00 for distillation head operating instructions).

6. Before running the method, position the controls of the Modular Printer as follows:

Control	Position
Mode Swith	Normal
Sampling Rate Switch	30
Range Swith	200
Decimal Switch	000

For details of Modular Printer Operation see Technicon Publication Number TA1-0278-10.

7. If necessary, alternate ranges may be obtained by utilization of the Std. Cal. control on the colorimeter.

8. The use of multiple working standards is only to establish linearity. For day to day operation, the 200 ug/l standard is recommended for instrument calibration.

9. After calibration, two control standards (separate from calibration standards) are also analyzed.

Quality Control

A field reagent blank and duplicate of one of the samples are analyzed with each group of samples. If twenty or more samples are analyzed, a minimum of two blanks and duplicates are analyzed.

The two control standards are re-analyzed along with a duplicate sample each hour. Data is only acceptable when the control samples and duplicates are within the control limits. Results are recorded in the AQC logbook.

The date of preparation of all reagents and standards are recorded in the AQC book. The Technicon Manufacturer's instruction are followed at all times as well as the daily readings of the calibration controls.

Calculations

ug/l Phenol = Reading from the printer in ug/l, times any dilution factor(s) applicable.

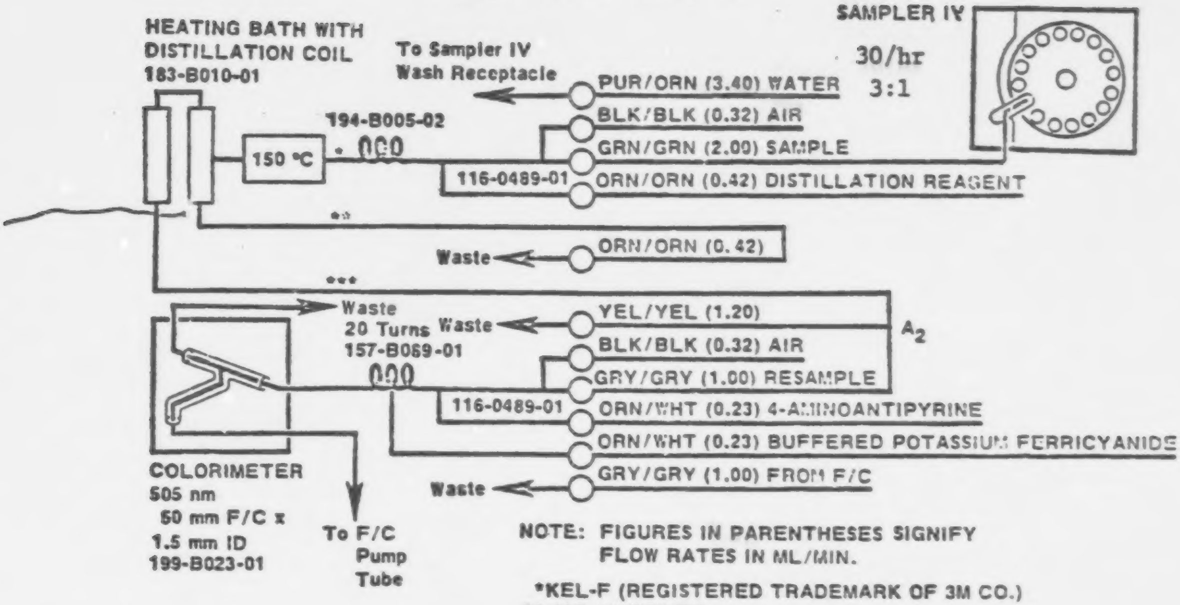
References

1. "Technicon Industrial Method Number 127-71W", Technicon Industrial System, Tarrytown, New York, October 1972.

2. Carter, Mark J., Huston, Madeleine T., "Preservation of Phenolic Compounds in Wastewaters", (Unpublished), Unites States Environmental Protection Agency, Region V, Central Regional Laboratory, Chicago, Illinois, 1977.

PHENOL

(Range: 0-500 µg/l)
MANIFOLD NO. 116-D115-01
PRE-DILUTION NO. 116-B214-03


HEATING BATH WITH DISTILLATION COIL
183-B010-01
To Sampler IV Wash Receptacle
SAMPLER IV
30/hr
3:1
PUR/ORN (3.40) WATER
BLK/BLK (0.32) AIR
194-B005-02
150 °C
GRN/GRN (2.00) SAMPLE
116-0489-01
ORN/ORN (0.42) DISTILLATION REAGENT
**
Waste
ORN/ORN (0.42)
***
Waste
20 Turns
157-B069-01
Waste
YEL/YEL (1.20)
A2
BLK/BLK (0.32) AIR
GRY/GRY (1.00) RESAMPLE
116-0489-01
ORN/WHT (0.23) 4-AMINOANTIPYRINE
ORN/WHT (0.23) BUFFERED POTASSIUM FERRICYANIDE
Waste
GRY/GRY (1.00) FROM F/C
COLORIMETER
505 nm
50 mm F/C x
1.5 mm ID
199-B023-01
To F/C
Pump
Tube

NOTE: FIGURES IN PARENTHESES SIGNIFY FLOW RATES IN ML/MIN.

*KEL-F (REGISTERED TRADEMARK OF 3M CO.)
**.100 ACIDFLEX
***.034 POLYETHYLENE

TECHNICON INDUSTRIAL SYSTEMS / TARRYTOWN, NEW YORK 10591
A DIVISION OF TECHNICON INSTRUMENTS CORPORATION

Analysis of Sediments and Other Solids for Oil and Grease
CRL Method Number 739

Scope and Application

This method is applicable to the measurement of freon extractable matter from sediments, sludges and other solids which contain relatively non-volatile hydrocarbons, vegetable oils, animal fats, soaps, waxes, greases and related compounds.

This method is not applicable to the measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oil are completely or substantially lost in the solvent extraction process.

This method is applicable in the range from 650 mg/kg to 100,000 mg/kg.

Summary of Method

The acidified sediment or solid sample is dried with magnesium sulfate monohydrate (avoid heating, which gives low results) and extracted with freon in a soxhlet apparatus for 4 hours.

Equipment

Extraction apparatus, soxhlet.
Vacuum pump or other source of vacuum.
Extraction thimble, paper.

Reagents

a. Hydrochloric acid, HCl, conc.
b. Magnesium sulfate monohydrate: Prepare $MgSO_4H_2O$ overnight

c. Freon (1,1,2-trichloro-1,2,2,-trifluoroethan), boiling point 47°C. The solvent should leave no measurable residue on evaporation; distill if necessary.
d. Grease-free cotton: Extract non-absorbent cotton with freon.

Procedure

In a 150 ml beaker weigh a sample of wet sludge, 20 ± 0.5 g of which the dry-solids content is known. Acidify to pH 2.0 (generally, 0.3 ml conc HCl is sufficient). Add 25 g $MgSO_4H_2O$. Stir to a smooth paste and spread on the sides of the beaker to facilitate subsequent removal. Allow to stand until solidified, 15 to 30 min. Remove the solids and grind in a porcelain mortar. Add the powder to a paper extraction thimble. Wipe the beaker and mortar with small pieces of filter paper moistened with freon and add to the thimble. Fill the thimble with glass wool or small glass beads. Extract in a Soxhlet apparatus, using freon, at a rate of 20 cycles/hr for 4 hours. If any turbidity of suspended matter is present in the extraction flask, remove by filtering through grease-free cotton into another weighed flask. Rinse flask and cotton with freon. Distill the solvent from the extraction flask in water at 70°C. Place the flask on a warm steam bath for 15 minutes and draw air through the flask by means of an applied vacuum for the final one minute. Cool in a desiccator for exactly 30 minutes and weigh.

Quality Control

One blank and one duplicate of one of the sediments are analyzed with each group of samples. If twenty or more samples are analyzed, a minimum of two duplicates are analyzed.

The analytical balance is calibrated and set at zero before each sample is weighed.

Calculations

Grease and oil as % dry solids

$$= \frac{\text{gain in weight of flask, g} \times 100}{\text{wt. of wet solids, g} \times \text{\% dry solids}}$$

REFERENCES

1. Standard Methods for the Examination of Water and Wastes, 14th ed., 1975 APHA-AWWA-WPCF, pp. 519-520.

2. EPA Manual, "Methods for Chemical Analysis of Water and Wastes" 1974 Office of Technology Transfer, Wash., D.C., pp. 226-228.

The Elutriate Test for the Analysis of Metals, Mercury, Cyanide, TKN, Total Phosphorus, Ammonia and COD

CRL Method No. 305

Scope and Application

This procedure is an estimate of the amounts of chemical substances which are exchanged (on a worst-case basis) when a sample of dredged sediment is shaken with four parts water collected near the sediment.

Summary of Method

One part of the wet sediment is added to four parts of process water followed by mechanical shaking for 30 minutes at maximum speed. Following one hour settling, the supernatant solution is centrifuged for 30 minutes, filtered through a pre-washed 0.45 micron membrane filter, transferred to a 12 ounce bottle and distributed to different sections of the laboratory for analysis of metals, mercury, cyanide and nutrients.

Equipment

Plastic bottles (12 oz and 2 oz)
Burrell Fast Oscillating Mechanical Shaker
Analytical Balance
Plastic Centrifuge Bottle

Reagents

See individual water procedures cited earlier in this manual.

Procedure

1. Place 50 ml of the wet well-mixed sediment sample and 200 ml of process water from the same area into a capped shaking bottle.

2. This mixture is shaken on the Burrell Mechanical Shaker for 1/2 hour at maximum speed.

3. Settle for 1 hour and pour approximately 200 ml of sample solution into a conical plastic centrifuge bottle.

4. Centrifuge at 15,000 RPM for 1/2 hour.

5. Filter through a pre-washed millipore 0.45 micron filter and transfer to a 360 ml plastic bottle.

6. Pour approximately 50 ml of sample into each of four 2 ounce (60 ml) bottles.

7. Preserve as follows:

Analysis		Preservative
bottle 1	Metals	500 Lamda (λ) (0.5 ml) of 8N HNO_3
bottle 2	Cyanide	500 Lamda (λ) (0.5 ml) of 1N NaOH
bottle 3	Mercury	500 Lamda (λ) (0.5 ml) of 2.5% $K_2Cr_2O_7HNO_3$ solution
bottle 4 (COD, TKN, TP, NH_3)	Nutrients	300 Lamda (λ) (0.3 ml) of 50% H_2SO_4

8. Following are the analysis procedures which are used for the parameters. These are the same procedures which are attached to CRL sediment procedures for Metals, Mercury, COD, TKN, TP and Ammonia. The completely automated cyanide procedure is only used for elutriates, not for sediments, (See CRL Method Number 357).

    Metals - CRL Method Nos. 600, 603, 606 - Arsenic, selenium and antimony by flameless atomic absorption.

    Metals - CRL Method Nos. 504 - 570 - plasma metals b ICAP (22 metals)

    Cyanide - CRL Method No. 357 - Total cyanide, automated distillation and colorimetry, (See pages 32-35 of this manual).

    Ammonia - CRL Method No. 312 - Automated phenate method.

    TKN/TP - CRL Method No. 465 (micro kjeldahl digestions followed by automated phenate).

    COD - CRL Method No. 342 - automated colorimetric.

9. The process water sample should be filtered, if necessary through a pre-washed, acid rinsed 0.45 micron filter.

10. It is then preserved according to the procedures in step 7 above or analyzed immediately using the procedures cited in step 8 above.

Quality Assurance

A blank and duplicate are analyzed with each group of samples. If twenty or more samples are analyzed 2 blanks and 2 duplicates are analyzed.

The balance is set to zero before and after each sample is weighed.

The manufacturers instructions are followed for all instruments.

Calculations

Same as for water. See individual method calculations.

REFERENCE

Ecological Evaluation of Proposed Discharge of Dredged or Fill Material into Navigable Waters, Interim Guidance for Implementation of Section 404 (b) (c) of Public Law 92-500 (Federal Water Pollution Control Act Amendment of 1972), Environmental Effects Laboratory, U.S. Army Engineer Waterways, Vicksburg, Mississippi, May 1976, Appendix A, pp. A1 to A7.

METHOD FOR ANALYSES OF PCB'S, PESTICIDES AND PHTHALATES IN SOILS AND BOTTOM SEDIMENTS
CRL METHOD NOS. 198 THRU 207

Scope and Application

The adsorption of chlorinated hydrocarbons on soils and muds is well documented. This procedure incorporates the recommendations of the Environmental Protection Agency's National Research Centers [1-5] to include the analyses of 25 pesticides, 2 phthalate esters and 4 polychlorinated biphenols (PCB) in mixtures. These are listed in Table I with their limits of detection. This method is recommended for use only by persons experienced in chromatographic analyses. The mention of trade names or commercial products here is for illustrative purposes only and does not constitute an endorsement for use by the Environmental Protection Agency.

Summary of Method

The soil or sediment sample is partially dried, sieved to 20-60 mesh, and extracted for 16 hours by soxhlet extraction with a mixture of 1:1 acetone/hexane (v:v). The extract is then concentrated, partitioned thru florisil and/or silicic acid as necessary for elimination of interferences and separation of various pesticide mixtures. Quantitative determination is affected via gas liquid chromatography employing electron capture or electrolytic conductivity detection and two or more unlike columns. Results are reported in milligrams per kilogram.

Interferences

The most common interference encountered with soil and sediment samples is sulfur. This interference can mask a major portion of the gas chromatogram. A method blank is required to monitor various possible contaminants in reagents and apparatus.

Apparatus and Materials

1. That outlined in the "Combined Method for Analysis of Pesticides, PCB's and Phthalates in Aqueous Media". [6]

2. Evaporating dishes - pyrex, 80 x 45 mm.

3. Oven-drying - 105°C.

4. Muffle furnace. 51 x 40 x 51 cm chamber size 66 - 1000°C temp range.

5. Desiccator.

6. Soxhlet extraction apparatus capable of holding cellulose extraction thimbles of 33 x 80 mm.

7. Distilled water, suitable for pesticide residue analysis.

8. Aluminum pans - approximately 9 x 12 x 2".

9. Aluminum foil.

10. Glass wool.

11. Sieves - meeting ASTM specification for 20 and 60 mesh size.

Procedures

1. Transfer the sediment into an aluminum pan and spread it to dry over a period of 1-4 days in a fume hood at ambient temperature. Pulverize sediment after drying, using a mortar and pestle.

2. As the final calculations will be made on a dry weight basis, the inorganic section will determine the percentage of total solids in each smaple using CRL Method No. 444, and provide the results to the Organic section.

3. Transfer the air dried sediment into a soxhlet apparatus between two layers of glass wool. The glass wool should be pre-extracted for 16 hours with 1:1 acetone/hexane (v:v). Extract the sample for 16 hours with 1:1 acetone/hexane (v:v).

4. Concentrate the extract to approximately 5 ml with a Kuderna Danish apparatus. Remove tube, rinsing joint with n-hexane.

5. The sample is now ready for initial gas chromatographic screening. This is conducted as described in the corresponding section for analysis of aqueous media. Colored material usually indicates necessity for florisil chromatography.

6. Interference appearing as peaks for high background as well as the general appearance and a knowledge of the sample source will determine whether treatment of the sample to remove chemical interference (commonly known as sample clean-up) is required. When these interfere with parameter measurement or pose a threat to gas chromatographic column life or detector sensitivity, proceed to section entitled, "Florisil Chromatography in Procedure for Aqueous Media".

Quality Control

1. Reagent blank - Beginning with the sample container a reagent blank is run with each set of 20 or fewer samples. The control limits are the detection limits listed in Table I listed below.

2. Duplicate and Spiked Samples - One sample is selected from each of 20 or fewer samples and divided into four aliquots after drying and mixing. Two of the four aliquots are spiked with an acetone solution (enough to wet the entire sample) containing approximately 10 ppm concentrations of the compounds of interest and the acetone is evaporated. All aliquots are then analyzed as real samples. The control limits are as follows: For duplicate analysis the relative percent difference (CRPD) should be less than 50% at an average concentration of 3x the above detection limit. The spike recovery should be calculated or described in appendix 1 of the CRL QC Manual and should be between 50 and 120%.

3. Each time a set of samples is run an extraction apparatus is charged with glass wool for a method blank.

Calculations

2. concentration of Pesticide and Phthalate components in sediments. The weight (ug) of sample per unit volume of extract (ml) is calculated by comparing peak areas of the sample chromatogram with that of a standard. This is accomplished with the aid of a gas chromatographic data system.[7]

$$\text{milligram/kg} = \frac{(A)\ (B)\ (V_E)}{(V_1)\ (W_s)\ 1000}$$

$$A = \frac{\text{nanogram standard injected}}{\text{standard peak area}} = \frac{ng}{mm^2}$$

B = sample peack area = mm^2

Vl = volume of sample injected (ul)

VE = volume of sediment extract (ul) from which sample was injected

Ws = weight in kg of sediment sample

3. Concentration of PCB's as Aroclor® mixtures in sediments.[8]

   A. When a simple Aroclor is present, the Aroclor® reference standards are compared to the sample. The areas of the unknown and corresponding the reference Aroclor are measured with the aid of a gas chromatographic data system. At least five peaks and the ratios are used to calculate the Aroclor concentration in the following manner:

$$\underline{\text{mg}} = \left(\sum_{i=1}^{n} \frac{Ai}{Bi} \right) \times \left(\frac{1}{n} \right) \times \left(\begin{array}{c} \text{concentration of standard} \\ \text{in } \mu\text{g per ml} \end{array} \right) \times$$

$$\left(\begin{array}{c} \text{final volume} \\ \text{of extract in ml} \end{array} \right) \times \left(\frac{1}{\text{sample in gm}} \right) \times \left(\frac{\%\ \text{solids}}{100} \right)$$

where: Ai = area of sample peak
Bi = area of corresponding standard peak
n = the number of peaks compared

B. For complex situations, the sample chromatogram is compared to each Aroclor® standard and a portion of the chromatogram is assigned to areas in which each of the Aroclors® predominate. The concentration of each PCB mixture in the sample is calculated using the major peaks in the region after peak areas from the interfering mixtures are factored out.

TABLE I

Limits of Detection for PCB's, Pesticides and Phthalates

Compound	Detection Limit (mg/kg)
2,4-D-isopropyl ester	5
di-n-butyl-phthalate	10
DCPA	2
Endosulfan I	2
Dieldrin	2
Endrin	3
Endosulfan II	2
di-2-ethylhexyl phthalate	10
Tetradefon	10
Treflan	2
Hexachlorobenzene	2
Lindane	2
beta-BHC	1
Heptachlor	1
Aldrin	1
Zytron	2
Isodrin	2
Heptachlor epoxide	2
gamma-chlordane	2
o,p'DDE	2
p,p'DDE	1
o,p'DDD	1
o,p'DDT	3
p,p'DDD	3
p,p'DDT	3
Mirex	3
Methoxychlor	5
Arochlor 1242	2
Arochlor 1248	2
Arochlor 1254	2
Arochlor 1260	2

These limits of detection must be demonstrated for the matrix of interest to be meaningful. The procedure for this is found in the section on Quality Control in Part I.

QUALITY ASSURANCE
PESTICIDES, PCB'S AND PHTHALATES IN SEDIMENT SAMPLES

1. Reagent blank - Beginning with the sample container a reagent blank is run with each set of 20 or fewer samples. The control limits are the detection limits listed in Table I above.

2. Duplicate and Spiked Samples - One sample is selected from each of 20 or fewer sample and divided into four aliquots after drying and mixing. Two of the four aliquots are spiked with an acetone solution (enough to wet the entire sample) containing approximately 10 ppm concentrations of the compounds of interest and the acetone is evaporated. All aliquots are then analyzed as real samples. The control limits are as follows: For duplicate analysis the relative percent difference (CRPD) should be less than 50% at an average concentration of 3x the above detection limit. The spike recovery should be calculated or described in appendix 1 of the CRL QC Manual and should be between 50 and 120%.

AQC SUMMARY SEDIMENTS

Parameter	Spike Level (mg/kg)	Average % Recovery
Aroclor® 1254	5	87
Tatradefon	5	55
Di-n-butyl phthalate	8	83
p,p'-DDT	5	74
Endosulfan II	5	71
p,p'-DDD	20	68
o,p'-DDT	3	74
Gamma Chlordane	4	85
p,p'-DDD	10	68
Endrin	3	67
o,p'-DDD	10	74
Dieldrin	10	72
Endosulfan I	10	73
o,p'-DDE	10	113
Heptachlor Epoxide	3	86
DCPA	6	70
di-ethylhexyl phthalate	20	78
Beta BHC	1	98
Lindane	3	77
2,4-D-isopropyl ester	10	101
Treflan	5	79
Aldrin	2	78
p,p'-DDE	3	80
Mirex	5	78
Isodrin	2	77
Heptaclor	1	89
Hexachlorobenzene	1	79

REFERENCES

1. L.E. Furguson, J.L. Ludbe, J.P. Wood, and J.W. Prather, J. Miss. Acad. Sci., 11, 219 (1965).

2. G.W. Barley and J.L. White, J. Agr. Food Chem., 12, 324 (1964).

3. M.W. Poirrier, B.R. Bordelon, J.L. Laseter, Environ, Sci and Technol. 6, 1033 (1972).

4. "Analysis of Pesticide Residue in Human and Environmental Samples" Environmental Protection Agency, Research Triangle Park, M.C. (1974).

5. T.A. Bellar and J.J. Lichtenberg, "Some Factors Affecting the Recovery of Polychlorinated Biphenyl from Water and Bottom Samples" presented at the symposium on Water Quality Parameters, Burlington, Ontario, Nov. 1973.

6. This procedure is adapted from:

   a. Methods for Organic Pesticides in Water and Wastewater 1971 and EPA publications appeared in Federal Register 38, 2758 (1973).

   b. Analysis of Pesticide Residues in Human and Environmental Samples, 1974.

7. J.H. Johnson, E.E. Sturino and S. Bourne, J. Environ. Sc: Health All. Sci. Eng. 2, 165 (1976).

8. R.G. Webb and A.C. McCall, J. Chromatogr. Sci., 11, 366 (1973).

PCB's PESTICIDES AND PHTHALATES
IN AQUEOUS MEDIA
CRL Method Nos. 144 to 183, 651 to 732 and 210 to 219

Introduction

The procedure is based on *Methods for Organic Pesticides in Water and Wastewater*, 1971 and EPA Publications from the National Environmental Research Centers.[1,2] This procedure differs from the referenced procedures in that the gas chromatographic step has been automated, and it has been expanded to include 44 pesticides, 5 PCB mixtures, and two phthalate esters. These parameters are listed in Table I along with their limits of detection in micrograms per liter. This method is recommended for use only by persons experienced in chromatographic analysis. The mention of trade names or commercial products here is for illustrative purposes and does not constitute an endorsement for use by the U.S. Environmental Protection Agency.

Summary

The procedure describes an effective co-solvent for efficient sample extraction. Elimination of non-pesticide interferences and separation of pesticide mixtures is accomplished with liquid column chromatography[1] (see Chart I). Qualitative and Quantitative determination is effected via gas liquid chromatography using electron capture and flame photometric detectors and two or more unlike columns. Results are reported in micrograms per liter.

Interferences

The analyst must be vigilant for contaminants in solvents, reagents, glassware, and other apparatus that comes in contact with samples as they will yield discrete erroneous artifacts in gas chromatograms. As it is not possible to describe all interferences which may be encountered in residue analysis, a method blank described herein is used to monitor interferences.

Apparatus and Materials

1. Gas Chromatograph equipped with:
    - a) glass lined injection port
    - b) electron capture detector
    - c) flame photometric detector (phosphorous mode)
    - d) potentiometric strip chart recorder compatible with detectors
2. Gas Chromatographic Materials:
    - a) tubing - pyrex (8' x 4mm ID)
    - b) glass wool - salanized
    - c) solid support - supelcoport (100-120 mesh)
    - d) liquid phases - expressed as weight percent of solid support:
        - i) 1.95% SP2250/1.5% SP2401
        - ii) 4% SE30/6% SP2401
3. Kuderna Danish Glassware:
    - a) synder columns - three ball
    - b) evaporative flasks - 500 ml
    - c) receiver ampule - 10 ml, graduated
    - d) ampule stoppers
4. Chromatographic Columns:
    Kontes or Ace 400 mm long x 10 mm ID with coarse fritted disc at bottom and teflon stopcock, 250 ml reservoir bulb at top of column (Kuderna Danish 250 ml evaporative flask).
5. Capillary pipets disposable (5 3/4 in.) with rubber bulb
6. Beakers, 100 ml and 500 ml
7. Erlenmeyers - 300 ml
8. Micro syringes - 10, 25, and 50 µl
9. Separatory funnel with teflon stopcocks, centrifuge tubes - 15 ml graduated, Erlenmeyer flasks - 125 ml and 3000 ml, 300 ml glass stoppered bottle
10. Graduated cylinders - 10 ml, 250 ml, and 1000 ml
11. Florisil - PR grade (60-100 mesh), purchase activated at 1250°F and store with glass stoppers or foil lined screw caps. Before use, activate each batch for 4 hrs at 450°C in foil-covered glass container. Determine elution pattern with parameters of interest before use with samples.

12. Silica gel - Davidson code 950-08-08-226 (60/80 mesh) or
    Bio Rad - Bio Sil A (100/200 mesh)
13. Culture tubes, 16 x 125 mm screw cap culture tubes, borosilicate glass with teflon-lined screw caps, 14 centrifuge tubes, 15 ml with teflon-lined screw caps

Reagents, Solvents, and Standards

1. Sodium sulfate - (ACS) granular, anhydrous, conditioned for 4 hours at 600°C
2. Sulfuric acid - reagent grade - 50% in distilled water
3. Sodium hydroxide solution - reagent grade 10 molar in distilled water
4. Diethyl ether - Nanograde, redistilled in glass, peroxide-free
   n-Hexane - pesticide quality (not mixed hexanes)
   Acetonitrite & methylene chloride, pesticide quality distilled in glass
5. Pesticide standards - those listed in Table I

Sampling

A. Sample Containers: Aqueous samples are collected in clean 1-liter narrow mouth glass quart bottles. The molded screw cap must have a teflon liner. Wide mouth glass jars are employed for mud samples. The caps are lined with aluminum foil previously washed with acetone and hexane.

B. Sample Collection: Surface water grab samples are taken by immersing the container and allowing it to fill up. A 500 gm sample of sediment is sealed in the above mentioned wide mouth jar.

C. Storage: Samples are extracted as soon as possible after collection, usually within two weeks.

Sample Preparation

1. Blend the sample if suspended matter is present. If organophosphate pesticides are to be measured, adjust pH to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10 normal sodium hydroxide.
2. Quantitatively transfer the sample into a two-liter separatory funnel.

Extraction

1. Add 60 ml of 15% methylene chloride in n-hexane (V:V) to the sample container, replace cap, shake for 1 minute, and pour the contents into the separatory funnel.
2. Stopper the separatory funnel and shake for 2 minutes.
3. Allow the organic layer to separate from the sample, then draw the water into the sampling container. Pour the organic layer into a 500 ml erlenmeyer flask containing 5 gm anhydrous sodium sulfate. Return the aqueous phase to the separatory funnel. Rinse the sample container with a second 60 ml volume of solvent; add the solvent to the separatory funnel, and complete the extraction procedure a second time. Perform a third extraction in the same manner with 60 ml of n-hexane.
4. Allow the organic phase to stand over sodium sulfate for at least one hour.
5. Concentrate the organic extract to approximately 5 ml in a Kuderna Danish evaporator on a hot water bath. The volume is first reduced to less than 4 ml using a stream of dry nitrogen, and then diluted to exactly 4 ml with n-hexane.
6. If analysis for organophosphorous pesticides is desired, the concentrated extract is divided into two 2-ml portions, A and B.

Analysis of Organophosphorous Pesticides (Compounds 1-16)

1. Spike portion A with phorate (2 µg) and inject 3-6 µl into a gas chromatograph equipped with a flame photometric detector.
   Gas Chromatographic Condition: An 8 ft x 6 mm OD x 4 mm ID coiled glass column packed with 4% SE30/6% SP2401 on 100-120 mesh Gas Chrom Q is used for the original analysis, and a 1.5% SP2250/1.95% SP2401 on 100-120 mesh Supelcoport is used for confirmation. Operating conditions are: inlet temperature 250°C, transfer unit temperature 250°C, detector temperature 240°C; and the oven programmed from 200° to 265°C, at 4° per min, nitrogen carrier at 60 ml/min.
2. The elution patterns relative to phorate are listed in Table 1.
3. Determine pesticide concentration by method outlined in "Calculations" section.

Analysis of Organochlorine Pesticides, Phthalate Esters, and PCB's (Compounds 16-45)

A. Qualitatively analyze the sample.

Approximately 5 µl of the concentrated extract (portion B of organophosphate pesticides are to be analyzed) are injected onto a gas chromatograph equipped with an electron capture detector.

Gas Chromatographic Conditions: A gas chromatograph equipped with a single inlet to dual column splitter, dual electron capture detectors and associated electronics, and dual 8 ft x 6 mm OD glass columns packed with (a) 1.5% SP2250/1.95% SP2401 and (b) 4% SE30/6% SP2401 both on 100-120 mesh Supelcon AWDCMS is employed. Operating conditions are: Injector temperature 250°C, column temperature 210°C, detector temperature 325°C, 5% methane:95% argon carrier with flow rate of 53 ml/min for column (a) and 50 ml/min for column (b).

Interferences appearing as peaks on high background as well as the appearance and a knowledge of the sample source will determine whether treatment of the sample to remove chemical interferences (commonly known as "sample clean-up") is required. If the parameters of interest are present with no interferences, proceed with quantitative analysis according to appropriate parameter as described below. When interferences complicate parameter measurement or pose a threat to gas chromatographic column life or detector sensitivity, proceed as follows:

B. Florisil Column Adsorption Chromatography

1. Place sodium sulfate into the chromatographic column to one-half inch.
2. Pour a slurry of 18 grams of Florisil in 80 ml n-hexane into the column. After settling the Florisil add one-half inch layer of sodium sulfate.
3. Pre-elute the column, discard the eluate just prior to exposure of the sulfate layer, quantitatively transfer the sample extract (portion B if organophosphate pesticides are to be analyzed) with subsequent washings of the sample container with n-hexane. Adjust the elution rate to about 5 ml per minute and collect two eluates.
4. Perform the first elution with 200 ml of 6% diethyl ether in

n-hexane (V:V), and the second with 50% di-ethylether in n-hexane (V:V).

5. Compounds 28-50 in the first eluate and compounds 17 thru 27 are contained in the second eluate.
6. Concentrate the eluates to 5 ml in the Kuderna Danish evaporator.
7. Analyze the second eluate by electron capture gas chromatography as outlined in "calculation" section. If PCB's and pesticides are present in the first eluate, proceed with silica gel adsorption chromatography.

C. Separation of PCB's from Pesticides with Silica Gel Adsorption Chromatography

1. Deactivation of Silica Gel: Place about 8 gm of silica gel per sample (prewashed with methylene chloride) in a glass dish or aluminum foil lined pan no deeper than ½ inch. Activate at 180°C for 16 hours. Transfer the silica gel to a glass stoppered bottle. When cool, add distilled water 1.0% by weight. Store the well sealed bottle in a dessicator prior to use. Silica gel can be effectively stored in this manner for several days.
2. Preparation of Chromatographic Column
    a. Fill a chromatographic column with n-hexane. Pack the lower one-half inch section of the column with anhydrous sodium sulfate.
    b. Weigh out 6 gm of silica gel and cover with 60 ml n-hexane.
    c. Carefully add the slurry to the column with gentle tapping making sure there are no air bubbles in the column.
    d. Turn stopcock to maximum flow rate.
    e. When the silica gel has settled, add sodium sulfate to form a one-half inch layer atop the silica gel.
    f. Turn off the stopcock just as the hexane enters the sodium sulfate layer.

   The column is now ready for use.
3. Chromatography of Sample
    a. Quantitatively transfer the sample (the 6% diethyl ether eluate (B) in n-hexane) concentrate onto the column with the reservoir

disconnected. As the last of the sample passes into the sodium sulfate layer, rinse down the internal wall of the column twice with ca 0.25 ml portions of n-hexane used to wash the sample container. Then assemble the reservoir onto the column.

4. Determination of Elution Volumes
   a. The elution volumes for pesticides and PCB's depend on a number of factors which are difficult to control; these include variations in:
      i) mesh size of the silica gel
      ii) adsorption properties of the particular batch of silica gel
      iii) polar contaminants in sample extract
      iv) dimensions of chromatographic column

   Hence, the optimum elution volume must be experimentally determined each time a variable is encountered. It is advisable to chromatograph a set of standards prior to each batch of samples to monitor any change in elution patterns.
   b. To determine the elution volumes add standard mixtures of Aroclors® and pesticides to the column and collect 10 ml sequential aliquots. Analyze each individual eluate by gas chromatography and determine the cut off volume for both the n-hexane (fraction E) and the acetonitrite, n-hexane, methylene chloride eluate (fraction F). At the CRL we find that all the PCB's are generally eluted in the first 45 ml of n-hexane along with hexachloro-benzene, mirex, aldrin, and heptachlor.

Quantitative Determination

Measure the amount of eluate and inject 5-10 μl into the gas chromatograph. If necessary adjust the volume of eluate to give a response which can be measured at the same attenuation as that for the standard.

1. Quantitation - Pesticides and Phthalates

   Measure the peak heights or areas of the known and the reference compound and calculate the concentration as follows:

$$\text{microgram/liter} = \frac{(A)(B)(V_E)}{(V_i)(V_s)}$$

$A = \dfrac{\text{ng standard injected}}{\text{standard peak area}} = \dfrac{\text{ng}}{\text{mm}^2}$

B = sample peak area = mm^2

V_i = volume of sample injected (μl)

V_E = volume of extract (μl) from which sample was injected

V_s = volume of water sample extracted (l)

Note: 500 ml of sample are used when the organophosphorous pesticides section is included and one liter when it is not.

2. At the Central Regional Laboratory, gas chromatograms of pesticides and phthalate esters are analyzed with the aid of a computerized gas chromatographic data system.[3] This system is readily incorporated into methods currently recommended by EPA for pesticide residue analysis and is available upon request.

3. PCB's

When a single Arochlor® mixture is present, quantitative reference standards (i.e. Arochlor® mixture) are compared with the unknown sample. An internal standard (Dieldrin® and Lindane®) is added to monitor the gas chromatographic data system. The retention time relative to the internal standards and peak areas are calculated by the data system.[3] The concentration of a PCB mixture in the sample is calculated by comparing at least three individual peaks of the unknown with corresponding peaks from the standard mixture on each of the two columns as follows:

$$\text{nanograms/liter} = \text{micrograms/kilogram} = \frac{V_i \; C_1 \; D_1}{V_s \; h \; D_2} = \sum_{i=1}^{n} \left[\frac{A_i}{B_i}\right]$$

V_i = final volume of the sample extract (ml) from which the sample is injected into the gas chromatograph

C_1 = concentration of the Arochlor® standard (ng/ml)

V_s = size of the sample (grams of soil or liters of water)

A_i= area of the individual sample peak

B_i= area of the corresponding peak from the standard

n = number of pairs of peaks used in the calculation

D_1 = area of the internal standard peak in the sample which does not interfere with peaks corresponding to the Aroclor® of interest

D_2 = area of corresponding peak from internal standard in the sample

4. For complex situations, the sample chromatogram is compared to each Aroclor® standard and a portion of the chromatogram is assigned to areas in which each of the Aroclors® predominate. The concentrations of each PCB mixture in the sample is calculated using the major peaks in that region after peak areas from interfering mixtures are factored out.

Sulfur is a common interference in the chromatographic fraction E. Sulfur removal is outlined in Appendix I.

When the concentration of PCB's is less than 100 ng/l, the samples are subjected to a perchlorination procedure.[5] A measured aliquot of the sample is transferred to a pyrex culture tube (previously muffled at 400°C) and the volume is reduced to 0.5 ml and then diluted with 2 ml chloroform. This solution is then concentrated to 0.2 ml with a stream of dry nitrogen at room temperature. A second 2 ml of chloroform is added and the volume is again reduced to 0.2 ml. This step is then repeated a third time followed by the addition of 0.5 ml antimony pentachloride. The tube is sealed with a cap lined with a teflon disc and heated for overnight at 175°C. The tube is then allowed to cool to room temperature, carefully vented (caution, HCl fumes), and slowly diluted with 6 ml of 2N hydrochloric acid. The aqueous solution is extracted with three 10 ml portions of hexane. The organic extracts are combined and back-washed with a 5 ml portion of 2N hydrochloric acid. The solution is transferred to a centrifuge tube, 5 drops of methanol are added, and the volume reduced to 2 ml. Hexabromobiphenyl is added as an internal standard and the solution analyzed by electron capture gas chromatography using a 6' x ¼" glass column packed with 4% SE-30/6% OV-210 operated at 245°C. This procedure affords greater sensitivity as the PCB is measured as a single peak. However, this procedure does not reveal the identity of the Arochlor® mixture or allow for any biphenyl present in the sample.

Although the perchlorination procedure is a valuable tool, it is subject to limitations. The analyst must be aware that biphenyl though not a PCB per se, can lead to erroneous results at low levels. The analyst should review the chromatogram of the sample before it is subjected to the perchlorination procedure. At CRL we express residues in terms of ppm decachlorobiphenyl when this procedure is used. When the procedure is used for quantitative confirmation, it can be expressed as a specific Aroclor® when a conversion factor is used.[6]

$$\frac{\text{DCB peak height of sample}}{\text{DCB peak height of standard}}\left(\frac{\text{ng standard}}{\text{injected}}\right)(Z) = \frac{\text{ng in sample}}{\text{injection}}$$

QUALITY CONTROL

A. Reagent Blank

A background or blank of each of the reagents or solvents used in this method are determined for each lot. The conditions to determine the background or blank must be the same as those used in the analysis. This is particularly needed with solvents. Sodium sulfate and chromatographic column packings are prone to contain phthalates in high concentration.

B. Method Blank

The method blank is determined by following the procedure with 1 L of distilled water, step by step to include all reagents and solvents, in the quantity required by the method. When this cumulative blank interferes with determination, steps must be taken to eliminate the interference. If this is not possible, the magnitude of the interference must be considered when calculating the concentrations of specific constituents in the samples analyzed and the limits of detection. One blank is analyzed with each set of ten or fewer samples.

C. Laboratory Control Standards

Laboratory control standards prepared in advance in sample bottles by adding acetone stock pesticide/PCB solutions (1.0 ml) to distilled water are analyzed with each set of 10 or fewer samples. The control limits for these samples are 50-150% recovery (measured) of the "true" value. The laboratory control standards are prepared separately from the instrument calibration standards so each audit also compares two sets of standards against one another.

D. Limits of Detection

These are estimated for each sample depending on chemical interferences found in that sample but usually the detection limits are less than 10 ng/l for the chlorinated hydrocarbon pesticides, 1 μg/l for the organophosphorus pesticides, 200 ng/l for PCB's using the traditional method, and 20 ng/l for decachlorobiphenyl.

CHART I.

Flow Chart for Extraction and Cleanup of
PCB's, Pesticides, and Phthalates

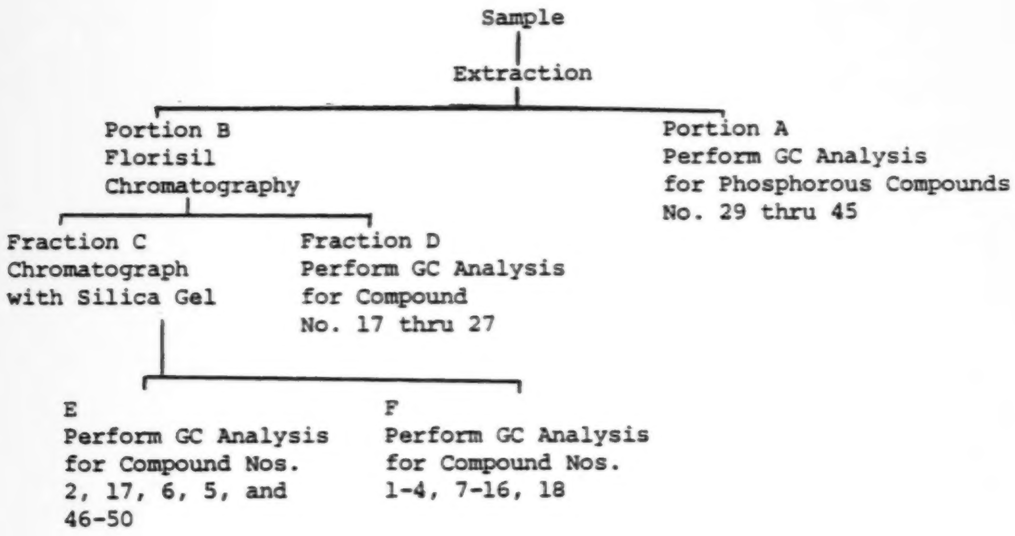

Sample
Extraction
Portion B
Florisil
Chromatography
Portion A
Perform GC Analysis
for Phosphorous Compounds
No. 29 thru 45
Fraction C
Chromatograph
with Silica Gel
Fraction D
Perform GC Analysis
for Compound
No. 17 thru 27
E
Perform GC Analysis
for Compound Nos.
2, 17, 6, 5, and
46-50
F
Perform GC Analysis
for Compound Nos.
1-4, 7-16, 18

TABLE I.

Physical Parameters for Parameters

Compound Number	Name	OV17/OV210 Relative Retention Time	SE30/OV210 Relative Retention Time	Limits of Detection µg/l
1	Treflan	0.44[b]	0.60[b]	0.004
2	Hexachlorobenzene	0.54[b]	0.50[b]	0.04
3	Lindane	0.70[b]	0.60[b]	0.004
4	β-BHC	0.77[b]	0.60[b]	0.004
5	Heptachlor	0.84[b]	0.84[b]	0.004
6	Aldrin	1.00[b]	1.00[b]	0.004
7	Zytron	1.15[b]	1.14[b]	0.01
8	Isodrin	1.26[b]	1.20[b]	0.006
9	Heptachlor epoxide	1.43[b]	1.40[b]	0.004
10	Gamma Chlordane	1.58[b]	1.47[b]	0.004
11	o,p'-DDE	1.68[b]	1.71[b]	0.006
12	p,p'-DDE	2.02[b]	1.87[b]	0.006
13	o,p'-DDD	2.35[b]	2.02[b]	0.006
14	o,p'-DDT	2.80[b]	2.20[b]	0.006
15	p,p'-DDD	3.00[b]	2.41[b]	0.006
16	p,p'-DDT	3.59[b]	2.86[b]	0.006
17	Mirex	5.58[b]	4.07[b]	0.01
18	Methoxychlor	6.62[b]	4.23[b]	0.02
19	2,4-D isopropyl ester	0.55[b]	0.86[b]	0.04
20	di-n-butyl phthalate	1.19[b]	1.17[b]	2
21	DCPA	1.48[b]	1.58[b]	0.006
22	Endosulfan I	1.72[b]	1.90[b]	0.01
23	Dieldrin	2.12[b]	2.29[b]	0.01
24	Endrin	2.54[b]	2.53[b]	0.006
25	Chlorobenzilate	3.54[b]	3.85[b]	0.01
26	Endosulfan II	3.10[b]	3.87[b]	0.006
27	di-2-ethylhexylphthalate	5.25[b]	5.39[b]	0.02
28	Tetrafidon	6.02[b]	7.50[b]	0.01
29	Phorate	1.00	1.0	2
30	Diazinon	1.3	1.3	0.02
31	Dyfonate	1.5	1.4	2
32	Ronnel	2.5	2.0	2
33	Dursban	2.9	2.3	2
34	Methyl Parathion	3.1	2.4	2
35	Malathion	3.4	2.5	2
36	Ethyl Parathion	4.1	2.9	2
37	DEF	4.7	3.3	2
38	Ethion	5.9	4.0[a]	2
39	Carbonphenthion	6.1	4.1[a]	2
40	Phencaptan	7.5	5.0[a]	2
41	EPN	8.4	5.5[a]	2
42	Azinphos Methyl	9.1	5.8[a]	2
43	Phosalone	9.3	6.0[A]	2
44	Azinphos	9.7	6.2[a]	2
45	Coumaphos	12.3	7.6[a]	2
46	Arochlor 1221			0.1
47	Arochlor 1242			0.1
48	Arochlor 1248			0.1
49	Arochlor 1254			0.1
50	Arochlor 1260			0.1

[a] Relative to Phorate - [b] Relative to Aldrin

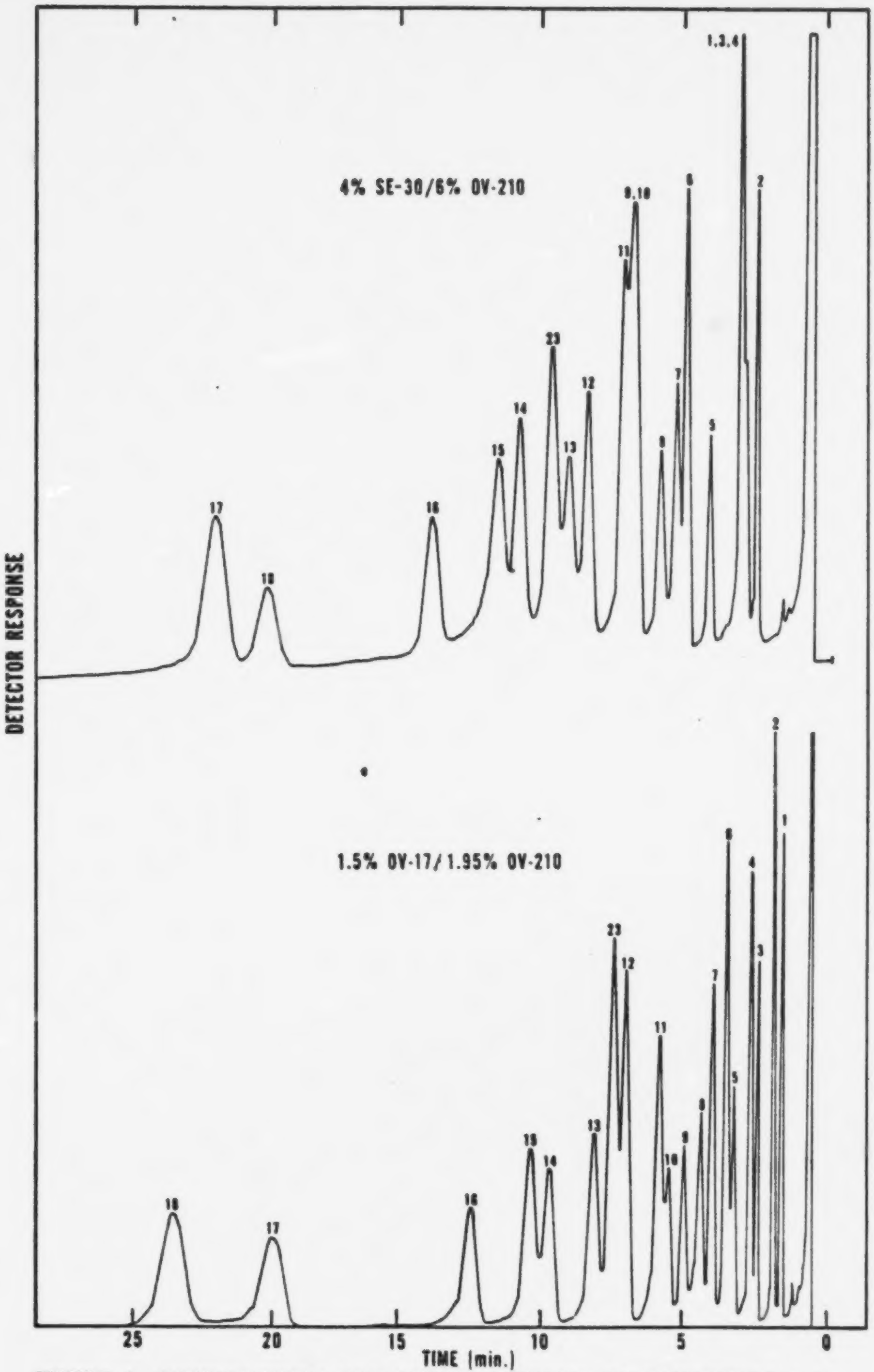


FIGURE 1. SIMULTANEOUS GAS CHROMATOGRAMS OF COMPOUNDS 1-18;
SEE EXPERIMENTAL FOR CHROMATOGRAPHIC CONDITIONS

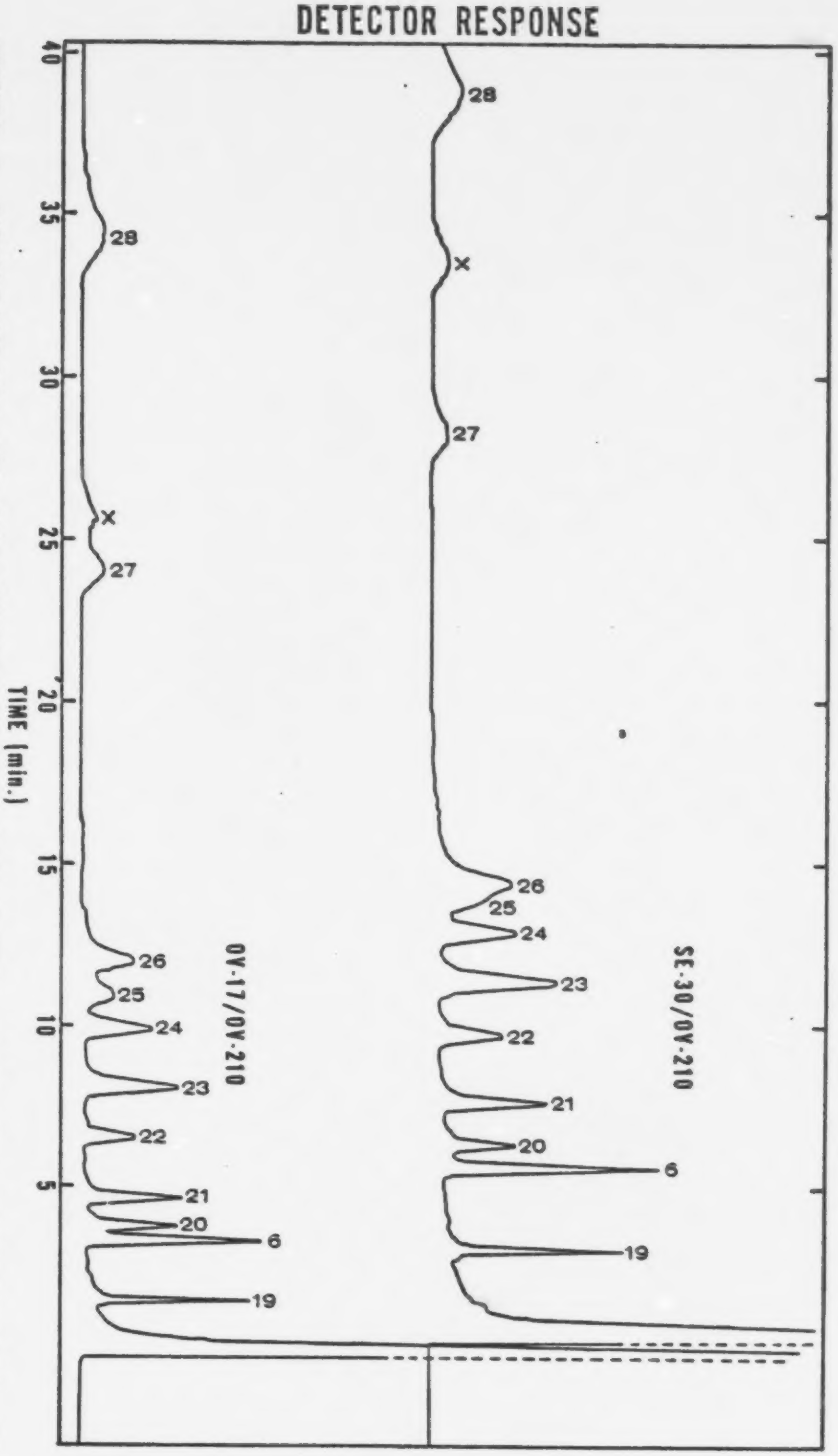


FIGURE 2. SIMULTANEOUS GAS CHROMATOGRAMS OF COMPOUNDS 18-28; SEE EXPERIMENTAL FOR CHROMATOGRAPHIC CONDITIONS

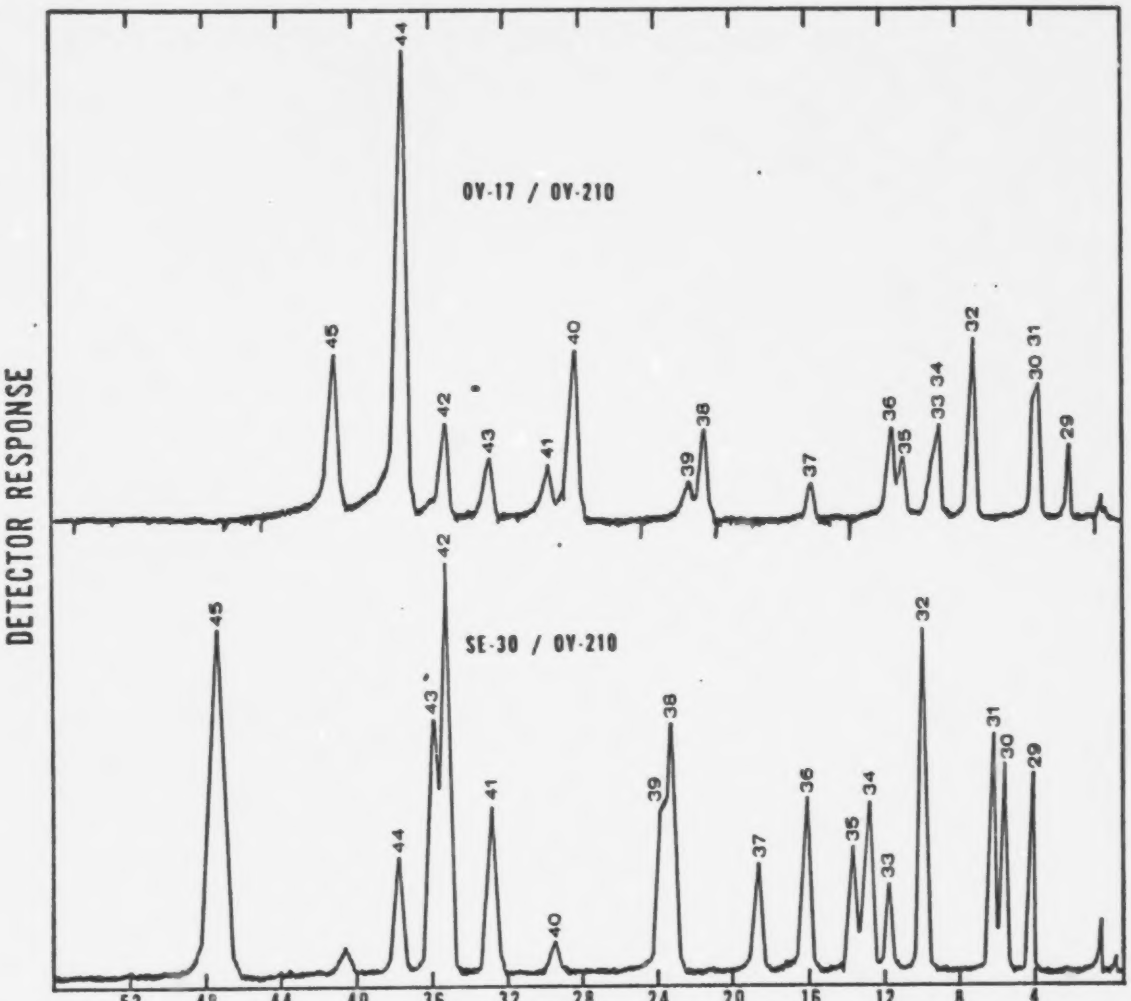


FIGURE 3. GAS CHROMATOGRAMS OF COMPOUNDS 29-45; SEE EXPERIMENTAL FOR CHROMALOGRAPHIC CONDITIONS

REFERENCES

[1] Federal Register 38, 2758 (1973) and references cited therein.

[2] *Analysis of Pesticide Residues in Human and Environmental Samples*, Environmental Protection Agency, Research Triangle Park, NC (1974).

[3] J. H. Johnson, E. E. Sturino, and S. Bourne. *J. Environ. Sci. Health - Environ. Sci. Eng. AII(12)*, 165 (1976).

[4] *Introduction to the G.C. Data System, Stored Method Version*, Perkin-Elmer Corp., Norwalk, Conn. (1971).

[5] W. J. Trotter, and S. J. V. Young. *J. Assoc. Offic. Anal. Chem. 58*, 466 (1973).

[6] J. A. Armour. *J. Assoc. Offic. Anal. Chem. 56*, 987 (1973).

[7] *Handbook for Quality Control in Water and Wastewater Laboratories*, Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio (1972).

APPENDIX I.

Sulfur Removal

Add a drop of metalic mercury to the eluate containing PCB's in a centrifuge tube. Stopper and place on a wrist action shaker. A black precipitate indicates presence of sulfur. After approximately 20 minutes the mercury may become entirely reacted or deactivated by the sulfur. Three treatments may be necessary to remove all the sulfur.

ANALYTICAL QUALITY CONTROL
Pesticide Unit, Organic Section

In order to insure validity in the analytical results, analytical quality control is to be performed not only on the total scheme, but also on each critical step of the scheme. In the analytical scheme for the chlorinated pesticides and PCB's given above, four steps may be classified as being the "critical steps." They are critical because if any of them fails, the whole scheme fails. The four steps are: 1) extraction, 2) Florisil liquid chromatography of the sample extract, 3) silicic acid liquid chromatography of a fraction collected from the Florisil column, and 4) the gas chromatographic analysis.

Sample Handling

In order to monitor the status of samples for PCB and pesticide analysis, all samples will be delivered to one person as assigned by the Section Chief. A folder will be prepared to contain data pertaining to the samples and to include: the data request form, and all extraction and chromatographic data.

The samples will be logged in the PCB and pesticide logbook in groups by the CRL designation number. The sample number and the parameters requested on the sample label will be checked against those listed on the data request sheet. Any discrepancies will be reported to the Section Chief and corrected prior to extraction.

The samples will then be turned over to the person assigned to extract them. Samples which are not extracted immediately will be stored in the refrigerator.

A set number will be assigned to each group of 10 samples and will be recorded by each sample in the Pesticide/PCB logbook by the person assigned to perform the extraction.

The pesticide group leader will prepare a series of 20 reagent blanks by adding distilled water to CRL sample bottles and placing these in a designated area. A second series of 20 samples will be prepared as laboratory control standards by adding one liter of distilled water and a measured amount of a pesticide/PCB stock solution to each bottle. These bottles will also be labeled and stored with the reagent blank samples. The laboratory control standards should be prepared completely independently of all instrument calibration standards and should contain all chlorinated hydrocarbon pesticides (20-200 ng/l), all organophosphorus pesticides (1-5 µgle), and Aroclors 1242 and 1254 (400-2000 ng/l). One reagent blank and one laboratory control standard should be analyzed with each set of samples.

If possible, reference standards should be run each quarter.

Control Limits

Control limits will be as listed below until further notice.

Reagent Blank:

a) Chlorinated hydrocarbon pesticides	10 ng/l
b) Organophosphorus pesticides	1µg/l
c) PCB's	100 ng/l

Laboratory Control Standards:

a) Chlorinated hydrocarbon pesticides	75-125% of True Value
b) Organophosphorus pesticides	75-125% of " "
c) PCB's	30-200% of " "

Summary of Results

The Pesticide Group Leader should establish audit control limits based on actual performance data as soon as possible.

The Section Chief should be notified about all audits out of control, and the action taken should be documented.

A summary of all QA results should be completed and reported to the CRL QA Coordinator through the Organic Section Chief as each series of 20 reagent blanks and laboratory control samples are about to be (15-17) completed.

TOTAL PCB'S AS DECACHLOROBIPHENYL

The total (usually 1 liter) is extracted, dried, concentrated, and purified with florisil as described by the Pesticide/PCB procedure. The purified extract is then perchlorinated v according to the attached procedure and the decachlorobiphenyl analyzed.

This method is very technique sensitive. An inexperienced chemist should not expect to obtain high quality data without considerable (1-2 months) practice with standard solutions.

QUALITY ASSURANCE

1) A reagent blank is analyzed to audit the total procedure. A second reagent blank is run to audit the perchlorination step. Antimony Pentachloride is usually contaminated with either biphenyl or PCB's in low concentrations. The control limit is 50 ng/l.

2) Laboratory control standards containing 1242/1016 and 1254 at 10-200 ng/l should be run with each set of 10 or fewer samples. The control limit is 50-150% recovery of measured PCB concentration.

3) One sample from each of 10 or fewer samples should be run in duplicate. The results should agree to within ± 50% ((difference/Average) x 100).

4) Since this method is so sensitive the quality assurance data should always be reported with the sample analytical data.

Previously the CRL has frequently experienced high reagent blanks when using this procedure so appropriate steps should be taken (check solvents, clean glassware, etc.) prior to starting a sample analysis.

Perchlorination Procedure

The solution of the sample to be perchlorinated is placed in a 15 x 85 mm disposable screw top culture tube, which has been muffled for at least six hours at 600°C. The sample volume is reduced to approximately one ml, two mls of chloroform are added, and the volume is again reduced to 0.2 ml - 0.1 ml. Dry air or nitrogen is used to affect these reductions in volume. The tube must not be heated or allowed to go to dryness during concentration or the yield of decachlorobiphenyl is reduced. If all of the hexane is not removed the reaction mixture turns black when the antimony pentachloride is added. Usually low yields are obtained from these solutions (50%).

One half ml of antimony pentachloride is added to the sample using a volumetric pipet. The culture tube is tightly capped with a teflon lined cap that has been fitted with an additional teflon disc liner. The tubes are placed in a Technicon Digestion Block at 175°C for a minimum of 4 hours. The digestion block is kept behind a safety shield in a fume hood. The tube must be handled with care as they become pressurized with chloroform vapors and HCl gas.

After cooling to room temperature, each tube is carefully opened in a fume hood. Rubber gloves and safety glasses are required. Two mls of 6 N (1:1) HCl are carefully added to the reaction mixture causing the evolution of HCl gas.

After gas evolution is complete and the mixture cools, four additional mls of 6 N HCl and two mls of hexane are added. The tube is capped and placed on a ferris wheel rotator for 15 minutes for shaking. We employ a moving rotator since twenty to thirty samples are usually run simultaneously. The aqueous phase is extracted a total of three times with two ml portions of hexane. The hexane extracts are washed one time each with two ml portions of 2N HCl and distilled water. A screw cap, 15 ml centrifuge tube is used for the washing as the lower aqueous phase is easily removed with a pasteur pipet. The hexane is then dried over anhydrous sodium sulfate. A pasteur pipet is used to agitate the solution to insure complete drying. The solution is then quantitatively transferred to a graduated 13 ml centrifuge tube to which has been added an appropriate amount of hexabromobiphenyl as an internal standard. An ebulation tube and five drops of methanol (to azeotrope and remaining chloroform) are added and the tube placed in a Kontes Tube Heating Block maintained at 80°C. The volume is reduced to 0.5 ml to insure complete distillation of chloroform.The solution is then brought up to an appropriate volume and analyzed by electron capture gas chromatography. A 6' x 1/4" glass column packed with the mixed phase 1.5% OV-17/1.95% OV 210 at 255°C and a carrier flow of 35 ml/min provides adequate resolution.

Method for the Analysis of "Priority Pollutants" in Solids and Bottom Sediments

CRL Method No. 1003

Determination of "Non Purgeable" Priority Pollutants in Sediments

Sample Preparation

1. Transfer the homogeneous sediment sample into an aluminum pan and spread it to dry over a period of 1-4 days in a fume hood at ambient temperature. Pulverize sediment after drying, using a mortar and pestle and sieve through 20 mesh sieve into a 60 mesh sieve. Sieve again with 60 mesh sieve and sediment retained on the 60 mesh screen is used for extraction.

2. As the final calculations will be made on a dry weight basis, it is necessary to determine the percentage of total solids in each sample. Weigh ca 5 gm of the homogenous sediment into a tared crucible. Determine the percent solids by:

    a. drying overnight at 105°C

    b. allow crucible to come to constant weight in a desiccator before weighing.

3. Transfer 20 g of the air dried sediment into a soxhlet apparatus between two layers of glass wool. The glass wool should be pre-extracted for 16 hours with 1:1 acetone/hexane (v:v). Extract the sample for 16 hours with 1:1 acetone/hexane (v:v).

4. Concentrate the extract to a ca 5 ml with a Kuderna-Danish apparatus.

    Remove tube, rinsing joint with n-hexane.

Separation of Acids from Neutral-Basic Compounds

The concentrated extract is transferred to a one l separatory funnel and extracted three times with 100 ml of 1.0N NaOH solution. (The NaOH solution is pre-extracted with methylene chloride to remove any organic compounds which may be present in the solution). The organic phase is dried over anhydrous sodium sulfate, concentrated to 4 ml in a Kuderna-Danish concentrator and transferred into two GC vials which are labeled as the base-neutral fraction (BN-I).

The aqueous extracts are returned to the separatory funnel, made acidic (pH3) with concentrated sulfuric acid and extracted three times each with 100 ml of methylene chloride. The extracts are combined, dried over anhydrous sodium sulfate, concentrated to 2 ml transferred into a GC vial and labeled as the acid containing fraction (A-I).

Quantification

The extracts are analyzed by gas chromatography/mass spectroscopy as outlined in the method for the analysis of priority pollutants in aqueous samples.

DETERMINATION OF PURGEABLE ORGANICS IN SEDIMENT

David N. Speis, Chemist

U.S. Environmental Protection Agency

Region II, Edison, New Jersey 08817

The analysis of volatile organic compounds in sediment poses challenging problems. Previous methods have been insensitive to low concentrations of volatiles in sediments. The reasons, behind this are twofold. Sediment analysis is usually limited to a 50 gm sample size for ease of sample handling. A liquid extraction of a sediment sample this large would be difficult. The large volumes of solvent required could not be concentrated by any solvent stripping technique without loss of the organics in question. Head space analysis is limited to small volume injections of low concentration resulting in a minimum detectable limit of 25 ppb "EMSL, Cincinnati, Ohio" (1977).

By modifying a Tekmar LSC-1 liquid sample concentrator to accommodate a 15 gram sediment sample and sample chamber heater, the analyst is able to thermally purge volatile organics from sediments. With this system, a minimum detectable limit of 0.1 ppb can be attained.

The purge and trap method is useful in the analysis of water samples for hydrocarbons and halogenated hydrocarbons. An inert gas (helium) is bubbled through the sample transferring those compounds favoring the vapor state from the aqueous phase to the gaseous phase. These gaseous compounds are then concentrated in a porous polymer trap at room temperature. (Figure 1) The trapped compounds are thermally desorbed into a gas chromatograph interfaced to an electron impact mass spectrometer, electron capture, or Hall electrolytic conductivity detectors "Bellar, Lichtenberg" (1974). (Figure 2).

PURGE MODE

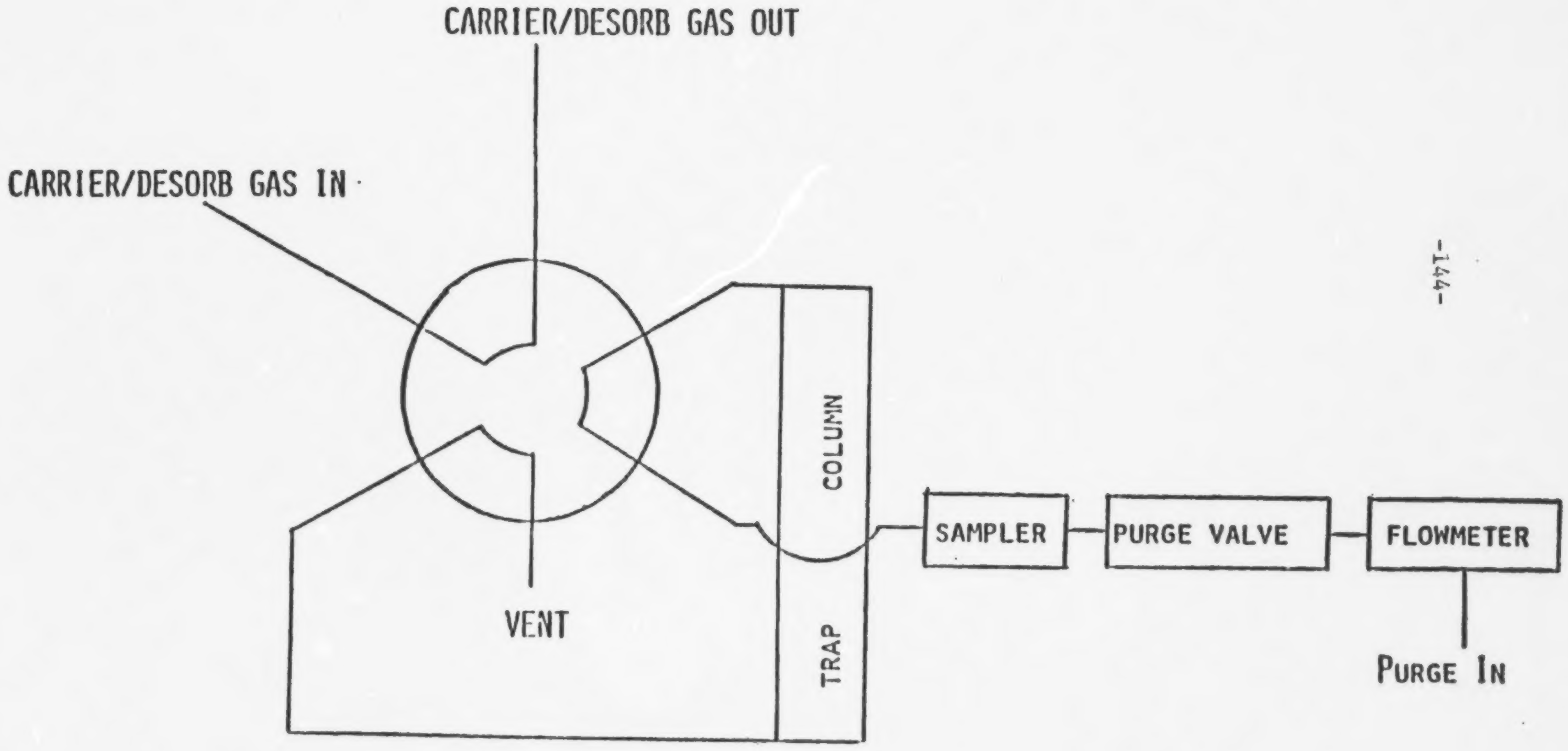

CARRIER/DESORB GAS OUT
CARRIER/DESORB GAS IN
VENT
COLUMN
TRAP
SAMPLER
PURGE VALVE
FLOWMETER
PURGE IN

FIGURE 1

DESORB MODE

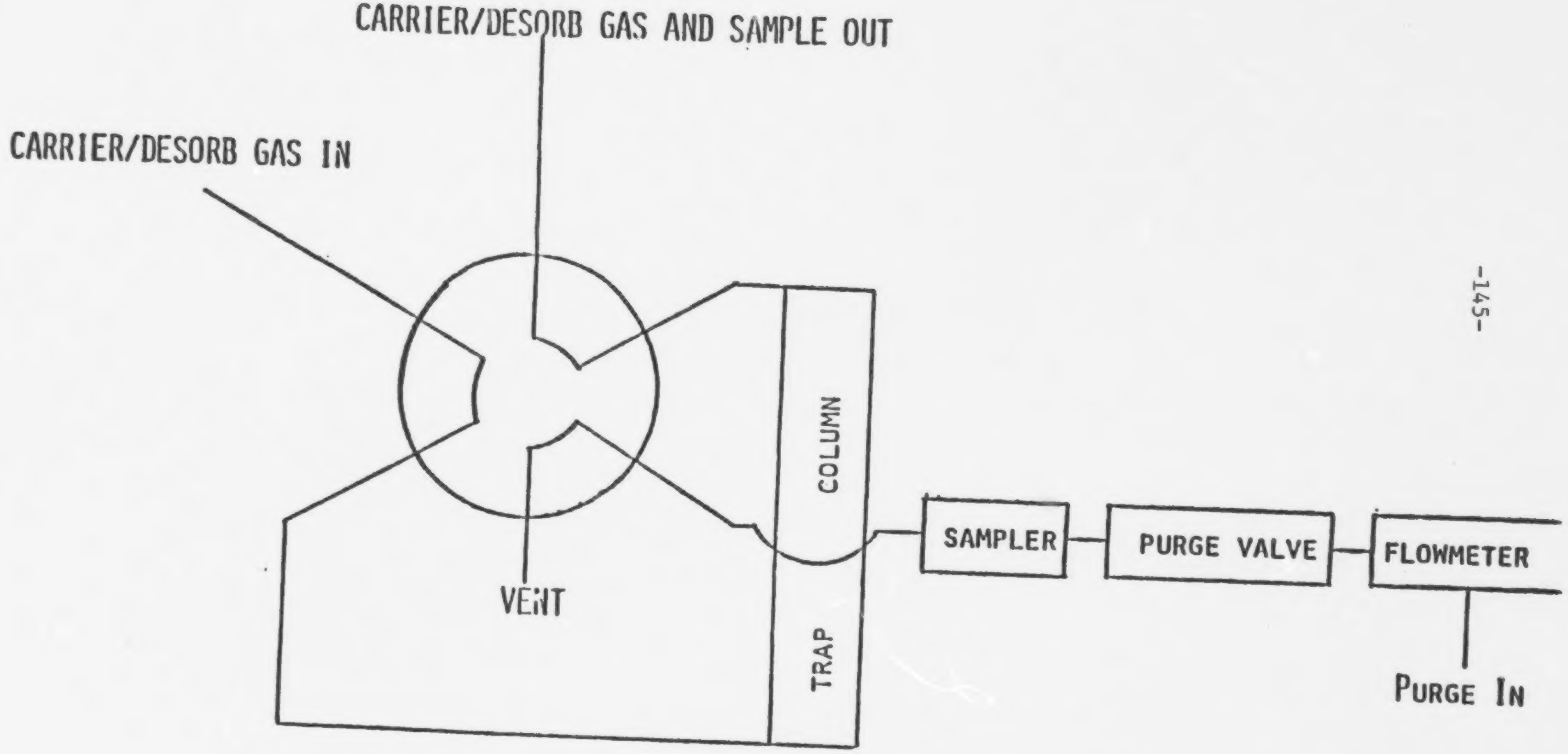

CARRIER/DESORB GAS AND SAMPLE OUT
CARRIER/DESORB GAS IN
VENT
COLUMN
TRAP
SAMPLER
PURGE VALVE
FLOWMETER
PURGE IN

FIGURE 2

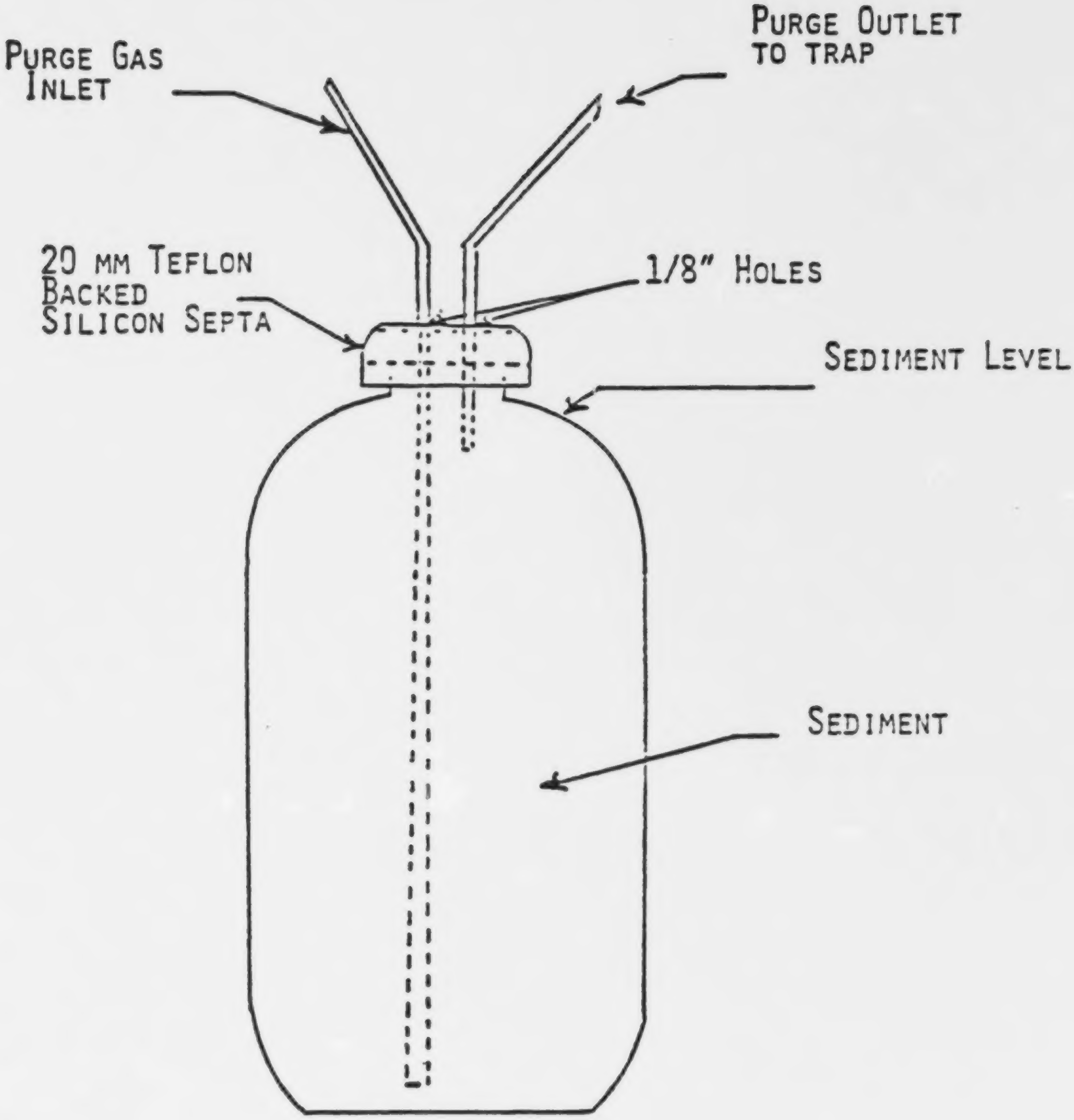
A Tekmar LSC-1 with modified sample container was interfaced to a Finnigan 3200 electron impact, gas chromatograph/mass spectrometer with a Systems Industries data system.

Sediment samples are collected in the field in pre-weighed Pierce (or equivalent) 20 ml hypovials with uncrimped aluminum seals and teflon backed septa. These vials have the capability of holding up to 15 grams of wet sediment. For best results, the vials should be filed to maximum capacity to reduce the amount of head space. The aluminum seals are crimped in the field after sample collection. All samples should be transported and stored at wet ice temperature and equilibrated to room temperature for weighing and analysis. Two holes are then drilled into the septum to allow the snug insertion of two 1/8" glass tubes to be used as a purge gas inlet and outlet. The purge gas inlet should be extended to the bottom of the septum vial. The purge gas outlet should extend 1/2" below the septum (Figure 3). The vial is wrapped in heating tape and the glass tubes are connected to the appropriate gas lines. The sample is then heated at 80°C for five minutes. At the conclusion of five minutes, the sample chamber is purged with helium for 4 minutes at a rate of 60 ml/min. This effectively traps volatilized organics on the polymer trap. The trapped organics are then desorbed onto the chromatographic column for analysis and data collection.

A pre-selected sediment whose consistency was that of a loose field soil, was muffled at 600°C to remove any volatile organics. This sediment served as a media for spiking. A solution of five volatile organics was prepared in methanol. This solution was injected directly into an empty septum vials to be used as a standard. This eliminates any matrix effects caused by the sediment so that an easy assessment of recovery can be made. Five dilutions of this standard were prepared in water. Ten mls of the diluted standard was pipetted into the septum vial containing 10-15 grams of pre-weighed sediment. The vial was sealed and allowed to stabilize for four hours. Five replicates of each concentration were analyzed as well as four unspiked sediments and four empty vials as blanks.

Minimum detectable levels obtained were 1.0 ng/15 grams of sediment (.07 ug/kg). Mean recoveries were calculated for each compound in each concentration group. Recoveries ranged from a high 52% to a low of 24%. The results are summarized in Table 1. The data was quite linear over the range of operation (Table 2). The lowest correlation coefficient was .934 for chlorobenzene; however, three compounds had values greater than .99.

MODIFIED SAMPLER


PURGE GAS INLET
PURGE OUTLET TO TRAP
20 MM TEFLON BACKED SILICON SEPTA
1/8" HOLES
SEDIMENT LEVEL
SEDIMENT

SCALE 2¼ = 1"

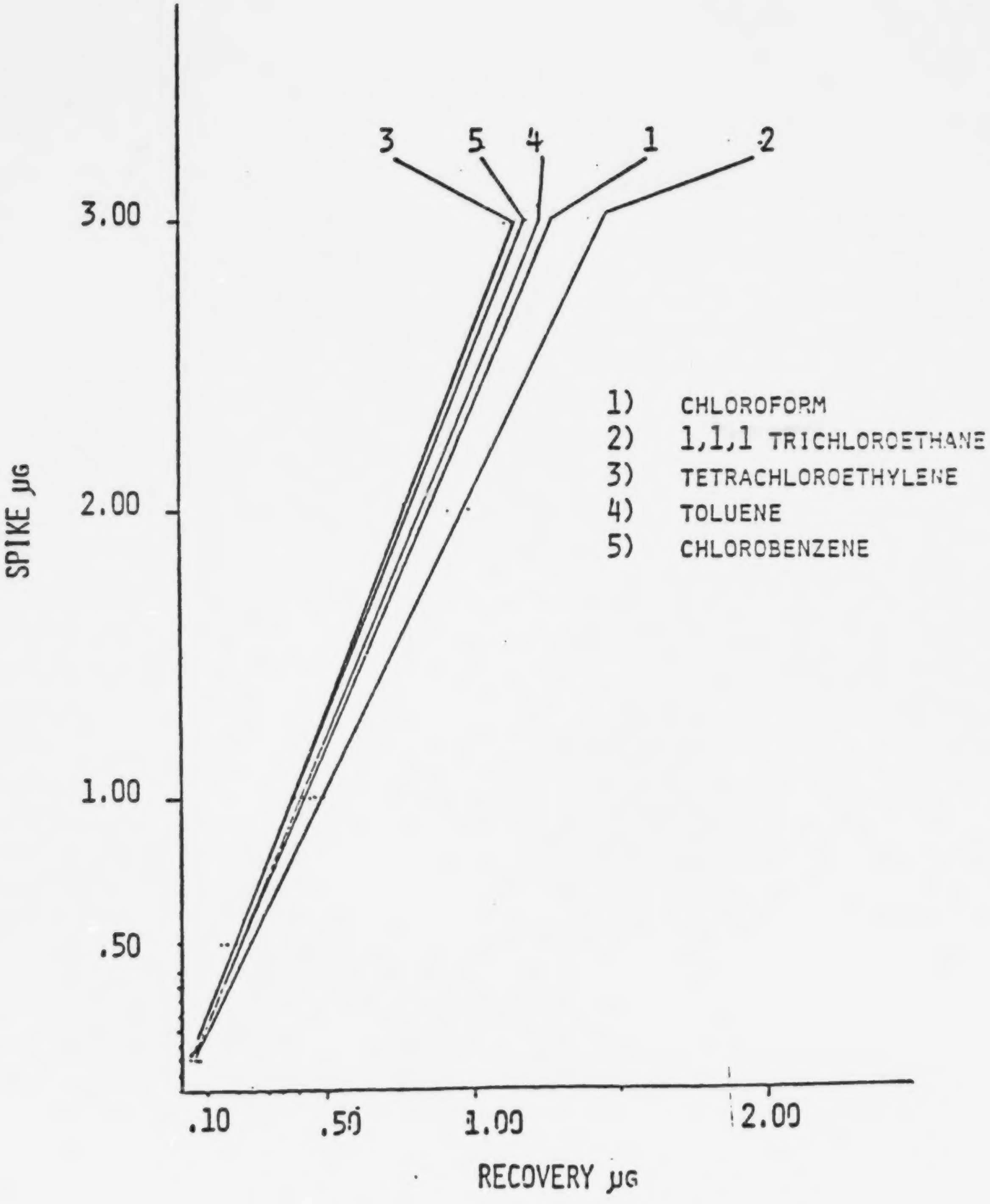
FIGURE 3

TABLE 1. RECOVERIES

	BLANK $\bar{x}$ NG	.100 UG SPIKE $\bar{x}$ RECOVERY	.500 UG SPIKE $\bar{x}$ RECOVERY	1.00 UG SPIKE $\bar{x}$ RECOVERY	2.00 UG SPIKE $\bar{x}$ RECOVERY	3.0 UG SPIK $\bar{x}$ RECOVERY
CHLOROFORM	1.0 (1.7)	.42 (.06)	.34 (.10)	.41 (.08)	.46 (.11)	.39 (.12)
1,1,1 TRICHLORETHANE	6.2 (2.7)	.52 (.05)	.44 (.10)	.50 (.04)	.50 (.09)	.46 (.10)
TOLUENE	6.4 (0.17)	.32 (.07)	.43 (.05)	.44 (.13)	.34 (.07)	.37 (.09)
TETRACHLOROETHYLENE	1.6 (1.6)	.32 (.09)	.24 (.06)	.37 (.08)	.34 (.07)	.39 (.08)
CHLOROBENZENE	3.8 (3.3)	.32 (.08)	.25 (.03)	.44 (.11)	.28 (.09)	.43 (.15)

N = 5 SAMPLES/COMPOUND CONCENTRATION
( )= STANDARD DEVIATION

TABLE 2 SPIKE RECOVERIES



Minimum detectable levels obtained using this sediment purge and trap procedure represent a 350 fold improvement in detection limits over that reported for head space analysis techniques. Although recoveries are on the low side, they are linear and reproducible. The results indicate that this can be a reliable method for detecting and determining low levels of volatile organics in sediments. This soil matrix represented the type of sample that would be taken as the result of an organic spill in an uncontaminated area. The matrix used was very difficult to purge of organics. The muffling served as an activation of a sediment that, otherwise, might not have held onto a purgeable compound so tenaciously. Higher recoveries would be expected from a contaminated unmuffled sediment. Limited available data on spiked environmental samples gave recoveries of 80-100% using this method.

References

Bellar, T.A.; Lichtenberg, J.J., and Kroner, R.C., Determining Volatile Organics in Microgram per Liter levels by Gas Chromatography. Journal American Water Works Association, Volume 66, No. 12, December 1974.

Sediment Sampling for Volatile Organics, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 2, 1977.

Residue, Total Non-filterable
(Suspended Solids)
CRL Method No. 441

Scope and Application

This method is applicable to drinking, surface, and saline water, domestic and industrial wastes.

The practical range of the determination is 10 mg/l to 20,000 mg/l.

Summary of Method

A well-mixed sample is filtered through a standard glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105°C. The filtrate from this method may be used for Residue, Total Filterable.

Definitions

Non-filterable solids are defined as those solids which are retained by a standard glass fiber filter and dried to constant weight at 103-105°C.

Sample Handling and Preservation

Non-homogeneous particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample.

Preservation of the sample is not practical; analysis should begin as soon as possible.

Interferences

Too much residue on the filter will entrap water and may require prolonged drying.

Equipment

Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder, Reeve Angel type 934-A or 984-H, Gelman type A, or equivalent.

Filter holder, membrane filter funnel or Gooch crucible adapter.

Suction flask, 500 ml.

Gooch crucibles, 25 ml (if 2.2 cm filter is used).

Drying oven, 103-105°C.

Desiccator.

Analytical balance, 200 g capacity, capable of weighing to 0.1 mg.

Procedure

Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water.

Remove all traces of water by continuing to apply vacuum after water had passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105°C for one hour. Remove to desiccator and store until needed. Weigh immediately before use.

Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml volumetric.

Depending upon the suspended solids concentration, a smaller or larger volume may be filtered. Wash the filter with 100 ml of distilled water.

Carefully remove the filter from the membrane filter funnel assembly. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103-105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

Quality Control

Duplicate samples are analyzed with each group of samples.

Calculations

Calculate non-filterable residue as follows:

$$\text{Non-filt. residue, mg/l} = \frac{(A-B) \times 1000}{C}$$

where:

A= weight of filter + residue
B = weight of filter
C = ml of sample filtered

Precision and Accuracy

Precision data are not available at this time.
Accuracy data on actual samples cannot be obtained.

Reference

This method is identical to the one in the EPA Manual of Methods for Chemical Analysis of Water and Wastes, 1974, Office of Technology Transfer, Washington, DC.